Characterisation and Optimisation of Gypsum Crystallization

Catherine H. Shannon

Department of Chemical Engineering, Cork Institute of Technology, Cork, Ireland.

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Characterisation and Optimisation of Gypsum Crystallization

Catherine Shannon

M.Sc. in Chemical and Process Engineering

1999
Characterisation and Optimisation of Gypsum Crystallization

Catherine H. Shannon

Candidate for the Degree of Master by Mode A (Research and Thesis)

Supervisors:
Mr. John O’Shea (CIT)
Dr. Aisling O’Gorman (CIT)
Mr. Peter Davies (ADM)

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April 1999
Abstract

Characterisation and Optimisation of Gypsum Crystallization

Catherine Shannon (B.Eng.)

Gypsum is produced as a by-product during the citric acid production process at ADM Ringaskiddy. The particle size and filterability of the gypsum has a critical bearing on the overall citric acid production rate. Prior to August 1996, research in the area of gypsum crystal optimisation at ADM had concentrated on the application of vortex mixing to perform the gypsum formation reaction. While the gypsum crystals produced with vortex mixing were found to be desirably clear of microcrystalline gypsum, the crystals were considerably smaller and more difficult to filter and wash. This research project sought to retain the advantages conferred by the vortex mixer but subsequently grow larger gypsum crystals in order to at least reclaim the design gypsum filtration capacity. The development of a comprehensive database enhanced the technical understanding of the gypsum production process. A pilot laboratory experimental rig was designed and constructed to simulate the plant results and facilitate intensive experimental trials. Experiments performed on the gypsum slurry (downstream of the vortex mixer) demonstrated that once the gypsum crystals have been formed, the crystal size cannot be increased. The most significant improvement in gypsum crystal size was obtained when the reaction was performed at a low specific gravity. The addition of impurities to act as habit modifiers did not succeed to influence the crystals as found by researchers in the phosphoric acid industry. Plant trials verified that the gypsum crystal size and filtration rates are much improved when the vortex mixer is off-line but the level of microcrystalline gypsum is higher. The low level of microcrystalline gypsum which is found with the vortex mixer on-line, was obtainable in the laboratory trials due to the adequate sulphuric acid dispersion system within the reactor.
Declaration

I hereby declare that the work detailed in this thesis is my own work, which was carried out at the Cork Institute of Technology and Archer Daniels Midland (ADM) Ringaskiddy between August 1996 and January 1998.

Catherine Shannon (B.Eng.)
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Summary

The purpose of this research project was to characterise and optimise the gypsum crystallization step of the citric acid production facility at ADM Ringaskiddy. The project work was carried out in Ringaskiddy from August 1996 to January 1998. Gypsum is produced as a by-product during the citric acid production process and the particle size and filterability of the gypsum, has a critical bearing on the overall citric acid production rate at ADM Ringaskiddy. Research in the area of gypsum crystal optimisation was ongoing in ADM since 1993. Prior to August 1996, the research had concentrated on the application of vortex mixing to perform the gypsum formation reaction. While the gypsum crystals produced with vortex mixing were found to be desirably clear of microcrystalline gypsum, the crystals were considerably smaller and more difficult to filter and wash. This research project sought to retain the advantages conferred by the vortex mixer but subsequently grow larger gypsum crystals in order to at least reclaim the design gypsum filtration capacity. The main objectives of the project were to:

- Develop a detailed technical understanding of the factors which influence the nucleation of gypsum crystals and the resultant filterability of gypsum.
- Characterise the existing gypsum crystallization reaction process.
- Define the existing gypsum production limitations.
- Design and construct a pilot laboratory experimental rig to simulate plant conditions and facilitate investigating trials.
- Evaluate options to overcome the current gypsum production limitations.

A literature search was carried out at the initial stages of the project. A review of general crystallization and precipitation process literature developed a thorough understanding of the actual crystallization process and associated terminology. A two-day foundation course on crystallization by AEA Technology also formed part of this research. Journal references provided details of previous research work that was carried out in the specific area of gypsum crystallization. Much of the literature provided a useful base for the development of a laboratory scale experimental programme.
A comprehensive database was developed in two stages over a 3 month period. The database development highlighted the large variation in process parameters, even over a 24 hour production period. The crystal habits of both calcium citrate and gypsum were detected and the trends and variations in crystal size throughout the gypsum production process were identified. Plant trials with the vortex mixer off-line, illustrated the increase in particle size attainable without the vortex mixer. An improvement in the gypsum filtration rate during these trials was confirmed as well as an increase in the quantity of microcrystalline gypsum present in the filtrate. Overall, the development of this database enhanced the technical understanding of the gypsum production process, identified the variation of crystal shape and size distribution along the formation path and provided an improved knowledge of the production limitation issues to be addressed throughout the project.

The design and construction of the pilot laboratory experimental rig was based on the desire to initially reproduce the plant results using the rig, with a view to progressing to intensive experimental trials in order to investigate the possible improvements available for the gypsum formation reaction and filtration steps. A single reactor was designed to mimic the two gypsum reaction vessels in the plant. The main reaction control parameters used were temperature and pH. Sulphuric acid was added to the reactor at a controlled flowrate via a dip-tube. The dip-tube was positioned just over the impeller to ensure adequate dispersion and mixing of the acid throughout the reactor. A hazard assessment was carried out on the rig prior to commencing any experiments. This assessment identified the potential hazards associated with the operation of the rig.

A series of optimisation experiments were carried out to optimise the laboratory rig set-up and operating conditions. The optimum height of the agitator from the bottom of the reactor was found to be 6cm. The sulphuric acid dip-tube was positioned over the blades of the impeller for the duration of the experimental trials. The optimum agitator speed found was 80% of the maximum. A sulphuric acid flowrate of 47.25 ml/min. was the optimum flowrate and was achieved by operating at 50% of the maximum pump speed. The optimum reaction temperature was found to be 80°C. Once the optimum set-up and operating conditions were determined, a
trial verified that the plant results were reproducible at these conditions. These conditions were held constant for the duration of the trial work.

The results obtained from the intensive experimentation period are summarised as follows:

- The pump transferring the calcium citrate slurry to the plant filters was not found to be the cause of the significant decrease in mean particle size between the calcium citrate slurry and the filter cake samples. The particle size decrease is actually caused by the presence of large grit particles in the slurry which settle out before reaching the filters and as a result, are not present in the cake samples.

- The addition of sulphuric acid to the gypsum reaction, even when the calcium citrate conversion was complete, was found to increase the gypsum mean particle size. This increase in mean particle size was proved to be a result of the additional acid being added and not due to residence time in the reactor.

- Residence time alone was not found to influence the gypsum crystal size. Therefore, extending the gypsum slurry capacity in the plant to increase the residence time of the crystals would not appear to be of benefit to the gypsum crystal size.

- A slight improvement in mean particle size and filterability results was observed when the reaction was performed using lower concentrations of sulphuric acid. The improvements did not appear significant enough to warrant further investigation.

- Microcrystalline hemihydrate material was successfully formed by using high H₂SO₄ flowrates and low agitation speeds to create 'hot-spots' within the reactor. The filtration of the slurry proved that the material was capable of getting through the filter cloth which, in the plant scale, would then be undesirably present in the refining end. A high possibility of filter cloth blinding also existed which would be detrimental to the gypsum filtration step.

- The absence of fine particles from the gypsum slurry had no significant effect on the particle size distribution. This suggested that the fine particles of hemihydrate gypsum in the presence of a dihydrate gypsum sample are not significant enough to be recognised by the Malvern instrument.
The reaction of $\text{H}_2\text{SO}_4$ with calcium citrate cake, produced low quality crystals with poor washing and filtration characteristics. The physical nature of the slurry also suggested handling difficulties which, in the large scale would pose a problem.

Trials with calcium citrate slurry suggested significant improvements in the gypsum crystals and hence improved filtration rates. Plate-like parallelogram-shaped crystals of gypsum were formed and the filterability result appeared to be much improved on the control samples.

The presence in the reaction, of citric acid mother liquor from the pannevis filtrate, did not have the same improved effect on the gypsum crystals as the calcium citrate slurry reaction. This suggested that some impurity present in the citric acid liquor prior to the calcium citrate filtration stage (but not present in the liquor remaining after the pannevis filtration), had a positive effect on the crystals.

Reactions using water to slurry the calcium citrate cake produced small, needle-shaped crystals.

Microscopic analysis of the initial trials using filtrate from the calcium citrate filtration step to slurry the calcium citrate cake, clearly illustrated that much better crystals were achieved (in agreement with those obtained using calcium citrate slurry). The Malvern analysis also supported the microscopic evidence of improved crystal size. Continuing trials rejected the theory that some impurity removed at the calcium citrate filtration stage, had a beneficial effect on the gypsum crystals. The improved crystals obtained previously were found to be a result of a much lower slurry specific gravity. The experiments performed with slurries of high specific gravity showed no improvement in crystal size or appearance.

Preliminary experiments in the presence of Sodium and Potassium Citrate impurities suggested a positive influence on the gypsum crystals. Further experimentation verified that the improvement was a result of high dilution factors.

Additional quantities of the cationic impurities present in the citric acid broth from the fermentation stage of the citric acid process were added to the reaction mixture over a series of trials. The addition of $\text{K}_2\text{SO}_4$ to the reaction system did not influence the gypsum
crystals. The addition of Na₂SO₄.10H₂O appeared to have a marginal negative effect on the gypsum produced. Experiments with high impurity contents of MgSO₄.7H₂O showed very significant changes in the particle size distributions but the slurry filtration rates did not change. The increase in particle size was actually found to be a result of particles of the impurity in the sample as opposed to gypsum crystal improvements. The addition of FeSO₄.7H₂O to the reaction system produced results similar to those obtained from the addition of MgSO₄.7H₂O. It was hoped that if the gypsum crystal habit was altered by any of these impurities, research into the identification of a substance similar in its habit modifying properties to the impurities tested, but effective in minute quantities could then be addressed.

- Impurities such as Fe₂(SO₄)₃.xH₂O and Al₂(SO₄)₃.16H₂O had a positive influence on the gypsum produced in the phosphoric acid process (Hasson et al., 1990), but they were not found to have the same effect on the gypsum produced in the citric acid process.
- The gypsum obtained from pure reactants appeared to be of better quality than the crystals normally formed.

From the intensive experimentation performed in this study, it appears that it is not possible to improve the gypsum crystal size and filtration rate while the vortex mixer is on-line. Experiments carried out on the gypsum slurry (downstream of the vortex mixer) demonstrated that once the crystals have been formed, the crystal size cannot be increased by any method. At this stage, as small crystals have been formed, their filtration rate is decreased. The reactions carried out using calcium citrate and sulphuric acid proved that the most significant improvement in gypsum crystal size was obtained when the reaction was performed at a low specific gravity. This reaction method would be undesirable in the plant however due to the increased evaporative loads on the downstream evaporators. The addition of impurities to act as habit modifiers did not succeed to influence the crystals as found by researchers in the phosphoric acid industry.

From the experiments performed, it was possible to achieve the same low level of microcrystalline gypsum in the laboratory as with the vortex mixer on-line. This led to the conclusion that with an adequate sulphuric acid dispersion system within the main gypsum
reaction vessel, the same effect should be achievable in the plant scale (i.e. maintain the low level of microcrystalline gypsum). At the end of the project, some research was carried out which briefly investigated the options available for an alternative sulphuric acid dispersion system. Some of the options available are:

- Extend the sulphuric acid dip-pipe to the most effective mixing point of the vessel.
- Increase the number of turnovers per minute in the vessel. This would require a larger agitator. Since the scope of agitator size increase is limited due to the size of the existing reaction vessel, a larger agitator would also require a larger vessel.
- Use two agitators in the existing reaction vessel to provide slightly better agitation.
- Separate off a small section of the vessel which would incorporate a small agitator. Use this small section of the vessel to add the sulphuric acid to the slurry. Use a weir-type arrangement to overflow the mixed slurry (i.e. gypsum) into the main reaction vessel and use the existing agitator to keep the solids in suspension.
- Use a series of dip-tubes to add the sulphuric acid to the existing tank. Use 90° bends at the end of the tubes and extend the discharge points just under the agitator blade tips where the mixing intensity would be highest. The use of multiple acid discharge points within the reaction vessel has already been successful for ADM Southport.

On completion of this project, it appears that the most beneficial modification to the gypsum crystallization step of the citric acid production process would be the removal of the vortex mixer and replace it with an improved sulphuric acid dispersion system within the reaction vessel. Plant trials have verified that the gypsum crystal size and filtration rates are much improved when the vortex mixer is off-line. Hence, if the level of microcrystalline gypsum can be reduced without using the vortex mixer, the current citric acid production limitations as a result of the gypsum filtration rate, should be essentially eliminated. It is recommended that any further work to be carried out in this area should concentrate on the development of a suitable sulphuric acid dispersion system with a view to reducing the quantity of microcrystalline gypsum being formed.
Chapter One

Introductory Chapter
1.1 Introduction

The purpose of this research project was to characterise and optimise the gypsum crystallization step of the citric acid production facility at ADM Ringaskiddy. The project work was carried out in Ringaskiddy over an eighteen month period. The main objectives of the project were to:

- characterise the existing gypsum crystallization reaction process
- define the existing gypsum production limitations
- design and construct a pilot laboratory rig to simulate plant conditions and facilitate investigating trials
- evaluate options to overcome the production limitations

This chapter provides an introduction to both ADM Ringaskiddy and ADM’s global network. The main product at ADM Ringaskiddy, citric acid, is described in terms of its production history, production process and scope of applications. The project background provides a brief introduction to the overall project, a statement of the objectives and an outline of the potential benefits.

1.2 Company Background

1.2.1 ADM’s Global Network

Archer Daniels Midland Company is an American Corporation with headquarters in Decatur, Illinois. The company, known as ADM, began in 1902 with a single flaxseed mill. Over the years and particularly in the last twenty five years, the company has grown aggressively to become one of the largest agricultural processing companies in the world. ADM is a leading processor of the world’s major cereal and oilseed crops, with over 200 manufacturing plants across the world. The company’s global network of production and distribution facilities, combined with its wide product range, make it a leading world-wide supplier of ingredients and additives to the food and beverage market.

In 1990, ADM expanded into the food chemicals market with the purchase of the Pfizer Inc. Citric Acid business and the commissioning of a major biochemical plant at Decatur. The
company's objective is to become a major producer of citric acid, amino acids and biochemical products for the food and feed industries.

Ringaskiddy, on Cork Harbour, is one of four major ADM plants in Europe which are part of the company’s global network. Its site at Hamburg is the largest multi-seed processing complex in the world. In the Netherlands, the soya processing facility at Europoort is also the largest of its type. ADM’s U.K. plant at Erith is the world’s largest softseed processing facility, producing edible oils from rapeseed and sunflower seed. These four plants and the network of smaller ADM operations within Europe, serve food and beverage manufacturers across the continent, supplying both locally processed ingredients and distributing other ADM products made in the U.S.A.

1.2.2 ADM Ringaskiddy

The major fermentation facility in Ringaskiddy marked 25 years of continuous operation in the summer of 1996. Since the plant came under ADM ownership in 1990, investment in substantial projects has significantly developed the site, strengthening its position as a major world producer of citric acid and citrates. Aimed at improving, expanding and automating the plant, ADM’s investment has produced one of the most modern manufacturing facilities of its type in the world.

The management, operation and maintenance of ADM’s plant at Ringaskiddy requires a wide variety of skilled personnel. These include, chemical, mechanical and electrical engineers, chemists, quality control technicians, maintenance craftspersons, plant operators, accountants, purchasing, shipping and warehousing specialists. The company employs 160 people directly and many more indirectly.

The ADM Ringaskiddy food chemicals operation comprises facilities for the manufacture of organic acid products including citric acid and gluconic acid. Within the plant are also such services as the powerhouse, waste water treatment plant, engineering workshop and offices. On site, three gas fired boilers can produce 125,000 lbs of steam every hour and the compressors can produce 90,000 cubic feet of air per minute. A 5 mega watt gas turbine
generator provides enough electricity to meet site requirements and the exhaust gas from the
turbine is utilised to raise steam in one of the boilers.

A key feature of the investment in the Ringaskiddy plant was the construction of an on-site
effluent treatment plant. The main waste stream or effluent from the plant is derived from the
production of citric acid and is almost entirely the residue of molasses used in the
fermentation process after the sugar has been utilised. The treatment plant generates energy
in the form of biogas (methane) which is used in the boilers to generate steam and hence
reduce fuel costs. The process removes virtually all the biological oxygen requirement of the
waste stream prior to discharge to the harbour.

A major feature of the site is the jetty which receives cargoes of molasses (up to 23,000 tons
at any one time) and sulphuric acid which comes in 4,000 ton lots, for use in the process.

The extensive facilities of the ADM plant at Ringaskiddy are used to produce fine chemicals
for sale in most countries of the world. The range of products includes citric acid hydrous
and anhydrous, sodium citrate, gluconic acid and glucono-delta-lactone. The main product is
citric acid which has moved gradually from being a speciality to a commodity type product
since production started in 1971. Therefore, the commercial success depends on three main
factors - selling price, cost of production and quality. Due to the competitive nature of the
market in which ADM chemicals are sold, cost reduction in the manufacturing of products is
a major management objective. ADM at Ringaskiddy is achieving production cost
effectiveness by continuous review of methods, raw materials and energy usage.

The process used in the production of citric acid is fermentation and the main raw material is
molasses. The molasses is fermented by using micro-organisms which convert the sugar into
crude citric acid which is then refined into the finished product. Fermentation is also the
process used to produce another ADM product, gluconic acid, but the main raw material used
here is dextrose (dextrose is a sugar product similar to glucose).

The application of the chemical products produced at Ringaskiddy is varied, with the bulk
being distributed for use in the food, drink and pharmaceutical industries. In the soft drinks
industry, citric acid provides the acid flavour and in the pharmaceutical industry, it usually
provides the ‘fizz’ typical of many pharmaceutical consumer products. In the food industry,
citric acid is used in the manufacture of boiled sweets to provide acidity and fruit flavours. Citric acid is also used in many food products where an adjustment to acidity is required. In the industrial side of industry, there are many uses of citric acid, particularly in the cleaning of high pressure boilers.

Applications of the other ADM products are as follows. Glucono-Delta-Lactone is used to assist in the accelerated maturing of certain salami-type sausage products, in some high quality baking powders and in specialised pharmaceutical products. Gluconic acid is used principally as a metal cleaning agent. Sodium citrate is used in detergents, as a food additive and in pharmaceutical formulations as an anti-coagulant.

1.3 Main Product - Citric Acid

Citric acid is a white or translucent solid with a chemical formula of C$_6$H$_8$O$_7$. The expanded formula is HOOCCH$_2$C(OH)(COOH)CH$_2$COOH. Citric acid is a tricarboxylic acid and in terms of IUPAC nomenclature, it is 2-hydroxypropane-1, 2, 3-tricarboxylic acid. It is also known as β-hydroxytricarballylic acid. It is a natural constituent and a common metabolite of plants and animals.

1.3.1 Production History

The history of commercial citric acid production can be traced back to the mid-nineteenth century in the U.K. when the Atlas Chemical Works in London started manufacturing the acid from lemon juice imported from Italy. The business was bought by John Bennett Lawes who, in 1869, sent one of his assistants to Palermo in Sicily to set up a plant to manufacture the citrate of lime from raw lemon juice and ship this, instead of the full juice, to the plant in London. In response to the increasing demand for citric acid, this process spread to all the Sicilian lemon growing districts, and also to other parts of Italy.

The previous plant manager from the Atlas Chemical Works left to set up another citric acid plant, Kemball Bishop, which was established in Bromley-by-Bow, London in 1871 with a production capacity of one and a half tons per week. The production of citric soon spread
with businesses developing in Germany, France and the United States. John Bennett Lawes’
business was eventually acquired by Kemball Bishop in 1913. Pfizer, who were the first to
commercialise citric production by fermentation, took a minority share-holding in Kemball
Bishop in 1936 and subsequently acquired the company in 1958. The Kemball Bishop plant
closed in 1971 and was followed by the start up of the Ringaskiddy plant. Pfizer’s world­
wide citric business was acquired by ADM in 1990.

Originally, citric acid was extracted from citrus fruits alone but the mounting pressure of
demand made this process uneconomical by the early 1900s. The first large-scale
fermentation was commercialised by Pfizer in 1923 using the micro-organism Aspergillus
Niger. Today, the main raw materials for citric acid production are carbohydrates such as
molasses and starches.

1.3.2 Production Process

Production involves fermentation techniques with micro-organisms converting the sugars into
citric acid. The citric acid broth produced from this fermentation is purified, concentrated
and crystallized into either the anhydrous or monohydrate form, depending on the
temperature. The acid is then sieved into fine, medium or coarse granules or powders.

In the 1980s, citric acid solution proved to be advantageous to the soft drinks and detergent
industries, enabling them to simplify production processes. Citric acid solution allows
greater flexibility in the production plant and ingredients can be added simultaneously rather
than sequentially. Further advantages include elimination of the need for on-site heating
boilers to predissolve the crystalline citric, no bags or pallets to dispose of, and reduced
labour and handling costs.

1.3.3 Scope of Applications

In addition to the various industrial and pharmaceutical applications, citric acid and its
citrates offer numerous functions which make them an important tool for a diverse range of
products right across the spectrum of the food and beverage industries. From sauces to soft
drinks, from canned fruits and vegetables to confectionery and desserts, citric acid products constitute an essential ingredient for food and beverage manufacture.

Citric acid fulfils a variety of functions imparting flavour, prolonging shelf-life and contributing to ease of processing, in a wide range of products. The citric acid and citrates produced at Ringaskiddy can be used as independent ingredients, in conjunction with each other, or with other types of food additives such as preservatives or antioxidants, to adjust their performance.

In both the food and beverage industries, citric acid is the preferred acidulant for producing a sharp 'acid' taste and enhancing the fruitiness of natural or artificial fruit flavours. When a high acid flavour is undesired, citrates may be used in conjunction with or in place of citric acid to create the desired effect. With regard to flavour, citric acid:

- Imparts a citrus tang to carbonated, still and powdered beverages and with citrate, it provides buffered acidity.
- Enhances fruit flavour and provides tartness in artificially or naturally sweetened confectionery.
- Contributes flavour in fruit sherbets and sorbets.
- With citrate, it reduces the after-taste associated with saccharin in carbonated drinks.

Citric acid and citrates have a preserving effect in certain foods. Citrates form stable complexes which aid the preservation of food by eliminating the trace metals that can contribute to their deterioration. With regard to shelf-life, citric acid:

- Increases the effectiveness of certain preservatives and reduces the heat processing requirements in fruit and vegetable products.
- Works with antioxidants to retard the development of off-colours in products containing fats and oils.
- Minimises discolouration and the development of off-flavour in shellfish.
- Can help to maintain freshness and prevent discolouration in prepared salads.

As well as the numerous benefits to the finished product in food and beverage manufacture, citric acid and citrates have valuable applications in promoting ease of production such as:

- Complementing the high-speed extrusion process in processed cheese.
- Accelerating the curing of cooked, smoked meat products.
- Aiding the carbonation retention in carbonated drinks.
Chapter One - Introductory Chapter

The list of applications for citric acid and its salts is diverse with small quantities being used in numerous other products not mentioned above.

Citric acid is accepted as a safe food additive in that the levels of citric and citrates required to create the desired effect in food products are safe for human health.

1.4 Background To Gypsum Crystallization Project

1.4.1 Introduction

The production of gypsum (see Section 2.3.1) is an integral step in the lime-sulphuric process for the production of citric acid. The gypsum produced is a by-product of the unit operation in which sulphuric acid and calcium citrate are reacted. The particle size and filterability of the gypsum produced has a critical bearing on:

- The filtration capacity required to adequately filter and wash gypsum.
- Subsequent refining filtration and crystallization characteristics.
- Energy consumption in subsequent refining operations.

The gypsum filtration stage of the citric acid process is a continuous bottleneck. Research in the area of gypsum crystal optimisation was ongoing in ADM since late 1993. Laboratory testing was extensive during this period although simulation of plant conditions had not been attempted. Prior to August 1996, development in the area of gypsum crystal optimisation had concentrated on the application of “fluidics” or vortex mixing to carry out the reaction between sulphuric acid and calcium citrate to produce gypsum. This vortex mixer replaced a traditional continuous stirred tank reactor which was previously used for the reaction. The addition of sulphuric acid to the conventional stirred tank reactor created “hot-spots” within the reactor. Due to the high temperatures at these spots, the product tended to burn which resulted in undesirable microcrystalline fragments. Removal of these small particles from the citric acid solution was therefore difficult.

The concept of vortex mixing was originally developed by the British Nuclear Industry and the vortex mixer project at ADM was piloted in association with a technical group derived from this industry. The process advantages of fluidic vortex mixing for the gypsum formation reaction are:
• Short mixing times - millisecond times achievable.
• Effective dispersion of small volumes into significantly larger volumes.

The mixing is completed before crystal nucleation (see Section 2.2.3) takes place, therefore a more consistent precipitate should be obtained. With vortex mixing, the problems of product burning leading to colour formation and a wide range of supersaturation values leading to particle size variation should be essentially eliminated.

The principal benefit arising from the application of vortex mixing was found to be the elimination of microcrystalline gypsum. Due to its amorphous nature, elimination of this gypsum type is desirable. It appeared in the subsequent filtrate as "slime" with adverse effects on the downstream filterability.

While the gypsum crystals produced with vortex mixing are clear of microcrystalline gypsum, they are of a considerably smaller mean particle size and are therefore more difficult to dewater and wash. In summary, the vortex mixer improved refining process efficiencies substantially but to the detriment of the gypsum filtration step. This impacted adversely on both filter capacity and yield.

This research project sought to retain the advantages conferred by the vortex mixer but subsequently grow larger gypsum crystals in order to at least reclaim the design gypsum filtration capacity. Substantial benefits would arise from such improvements in crystal size because:

• Improvements in filtrate clarity enable reductions in process recycles which in turn lead to yield improvement.
• Improvements in the rate at which the slurry can be filtered confer valuable additional capacity to this operation and also offer considerable reductions in wash water with downstream steam savings.
1.4.2 Potential Benefits

The potential benefits arising from this research are as follows:

- Larger and more uniform crystals would permit higher gypsum filtration rates due to the use of a more open filter medium. This would debottleneck the gypsum filtration step and allow a higher specific gravity of the filtrate (known as *sour filtrate*) going forward to the refining stage. Less water could be used to wash the gypsum cake which would also reduce the evaporative load on a downstream evaporator.

- Downstream filtration cycles would be consistently larger and therefore less frequent. Hence, dilution of the citric acid solution through washing would also be less (say 20% less washings), resulting in additional steam savings.

- If the clarity of the filtrate from the gypsum filtration stage (sour filtrate) is improved, it can be sent forward for refining without further polishing (removal of minute particles) on filters known as *precoat filters*. This gives considerable yield savings. The elimination of sour filtrate polishing would reduce the evaporator load with substantial annual savings. If the sour filtrate was not being polished, reduction in the precoat filters running time would result. The precoat filter cake is neutralized by caustic soda before discharge, therefore annual caustic soda savings would also be achieved.
Chapter Two

Literature Review
Chapter Two - Literature Review

2.1 Introduction

This chapter forms a review of the literature researched throughout the project. A review of general crystallization literature was initially carried out in order to form a thorough understanding of the actual crystallization process and the associated terminology. Emphasis was then directed towards the more specific area of "gypsum crystallization". Much of the available literature concerning the production of gypsum crystals, refers specifically to the gypsum produced as a by-product of the phosphoric acid process. However, some literature directly related to gypsum produced from the citric acid process was also sourced and reviewed. In addition, literature relating to the influence of additives and impurities on gypsum crystals was reviewed, as well as literature dealing with the general production of gypsum (as opposed to by-product gypsum).

Much of the literature reviewed in this chapter provided a useful base for the development of a laboratory-scale experimental programme. Details of the experimental programme followed can be found in Chapter 6.

2.2 General Crystallization Literature

2.2.1 Introduction

Crystallization is the conversion of a substance or several substances from an amorphous solid, liquid, or gaseous state to the crystalline state. It is a separation and purification technique employed to produce a wide variety of materials. It may be defined as a phase change in which a crystalline product is obtained from a solution. The main objective of a crystallization or precipitation process is to obtain a product with a large median crystal size, a small coefficient of variation of the particle size distribution, a regular and compact crystal shape, and a high degree of purity.

Crystals are solids in which the atoms are arranged in a periodic repeating pattern extending in three dimensions. The crystals can be classified into seven crystal systems: regular, tetragonal, orthorhombic, monoclinic, triclinic, trigonal and hexagonal.
2.2.2 Crystallization Mechanisms

For crystals to be formed, or existing crystals to grow, a liquid phase must be supersaturated. The most commonly used basic techniques for creating supersaturation in the solution phase include cooling, evaporation, dilution and chemical reaction. Cooling and evaporative crystallization are the crystallization processes involving solution cooling or solvent evaporation as methods of creating supersaturation. In vacuum crystallization, flash vaporization is used to obtain supersaturation. The process of adding a displacement agent/diluent to reduce the solubility of the dissolved substance and thus lead to supersaturation, is known as salting-out or dilution crystallization. In reaction crystallization, two or more reactants react together to form a product which is then supersaturated and crystallizes out.

Crystallization from a solution is the crystallization of only the dissolved substance, while melt crystallization applies when all components change from the liquid to the solid phase. Freeze crystallization refers to the concentration of the dissolved substance in a solution (i.e. crystallizing the solvent, not the dissolved substance as in solution crystallization). Most industrial crystallization equipment employ some form of agitation or circulation of mother liquor or suspension to ensure the uniformity of suspension and/or supersaturation.

Crystallization from solution can be seen as a two-step process. The first step is the phase separation and the second step is the growth of these crystals to larger sizes. These two processes are known as nucleation and crystal growth. It is the relation of the degree of nucleation to crystal growth that controls the product crystal size and size distribution and is therefore, a crucial aspect of industrial crystallization processes.

2.2.3 Nucleation

The process of nucleation involves the formation of new crystals in a crystallizing environment. Supersaturated state of solution is a prerequisite, but not a sufficient cause for a system to begin to crystallize, since a large number of minute entities known as centres of crystallization, embryos or seeds first exist in the solution. In practice, the formation of new crystals may result from any one, or a combination of two different mechanisms classified as
primary or secondary nucleation. The various recognised modes of nucleation are shown in Fig. 2.1.

![Nucleation Mechanisms](image)

Primary nucleation occurs in the absence of crystalline surfaces while secondary nucleation involves the active participation of these surfaces. Two types of primary nucleation can be identified; homogeneous nucleation in which formation of the solid phase is not brought about by the presence of any solid phase, and heterogeneous nucleation, where formation of the new solid phase particles is catalysed by the presence of a foreign solid phase.

Homogeneous nucleation rarely occurs in practice, however, it forms the basis of many nucleation theories. Heterogeneous nucleation is usually induced by the presence of foreign particles rather than spontaneously produced. Nucleation can often be induced by agitation, mechanical shock, friction and extreme pressures within solutions and melts. The presence of crystals in the supersaturated solution (i.e. seeding) usually causes nucleation at a much lower level of supersaturation than in their absence. The presence of impurity in a system can have a profound influence on the nucleation behaviour and there often appears to be a threshold concentration of impurity, above which this effect may be weakened.

Secondary nucleation is the mechanism by which formation of the solid phase is initiated by the presence of solid phase of the crystallizing material itself. It involves the prior presence of crystals of the material being crystallized and its interaction with the environment (i.e. crystallizer walls, impellers etc.). The categorization of the different secondary mechanisms in Fig. 2.1 is somewhat arbitrary, but all the mechanisms involve the surface of a growing crystal. Nucleation by fluid shear results when the fluid velocity relative to the crystal velocity is large and some of the “adsorbed layer” is removed. The adsorbed layer, being nearly entirely solute, will nucleate if the clusters are sufficiently large. Nucleation by some
form of fracture process occurs in systems that produce crystals that break easily, where the suspension is very dense, and where the suspension is subjected to violent agitation or high-velocity pumping. Nucleation by attrition is basically fracture of a lesser degree and results from crystal-crystal interaction at high suspension densities as well as from crystal-apparatus contact. Needle breeding occurs because of dendritic growth (see Section 2.2.5) on crystals. Contact nucleation is the most important source of nuclei in mixed suspension and results when crystals contact the agitator, pump, flow lines or other crystals.

The supersaturation, rate of cooling, degree of agitation and the presence of impurities are factors which influence these processes. In particular, the presence of impurities in a system can affect nucleation behaviour very considerably. The presence of small amounts of colloidal substances can suppress nucleation in aqueous solution and certain surface-active agents also exert a strong inhibiting effect. Traces of foreign ions, especially Cr$^{3+}$ and Fe$^{3+}$, can have a similar action on inorganic salts. It appears that the higher the charge on the cation, the more powerful the inhibiting effect. Also, there often appears to be a 'threshold' concentration of impurity above which the inhibiting effect may actually diminish. (Mullin, 1993).

The period of time that usually elapses between the achievement of supersaturation and the appearance of crystals is known as the induction time or period. It is considerably influenced not only by the initial conditions and process conditions, like supersaturation, state of agitation, presence of impurities, temperature, and seeding, but also by the measurement technique.

### 2.2.4 Crystal Growth

Crystal growth is the part of the crystallization process where the nuclei grow larger by the addition of solute molecules from the supersaturated solution. This, along with nucleation, controls the final particle size distribution obtained in the system. The conditions and rate of crystal growth also have a significant impact on the product purity and the crystal habit (see Section 2.2.5).
All crystal growth rates are said to be particle size dependent in that they depend on the size and size range under consideration. For macrocrystals, the effect of size may be quite insignificant but the situation can change dramatically for crystals of microscopic or sub-microscopic size.

The presence of impurities in a system can have a profound effect on the growth of a crystal. Some impurities can suppress growth completely, some may enhance growth, while others may exert a highly selective effect, acting only on certain crystallographic faces and therefore modifying the crystal habit. In some cases, impurities can exert an influence at very low concentrations while others need to be present in relatively large amounts before having any effect.

2.2.5 Crystal Habit

The external appearance of the crystals is referred to as the crystal habit, crystal shape or crystal morphology. The habit of a crystalline material is defined as the common or characteristic form or combination of forms in which it crystallizes. The habit of any crystalline material depends on the environment in which the crystals are formed and on the rate of crystal growth. Crystal habit is a function of both the internal structure of the crystal and the external conditions of growth. Under most conditions, the shape of a crystal is determined by kinetics rather than thermodynamics and the resulting habit is termed the “growth” as opposed to the “equilibrium” habit.

The habit of crystals obtained from an industrial crystallization process can have a major impact on a number of important properties relating to the slurry and the dry product. Crystal habit will affect the rheological properties of the suspension, the filtration efficiency, the bulk density of the solid, and the flow properties of the solid. Therefore, the control of crystal habit along with crystal size distribution is an important part of industrial crystallization processes.

It is extremely difficult to predict the shape of crystals due to the variety of influencing parameters. In industrial crystallization, the shape of crystals can be influenced by:
• Properties of the crystalline solid
• Properties of the solution
• Operating mode and conditions.

The shape and size of crystals are influenced by the presence of specific admixtures or an excess of one of the constituent ions, temperature, system pH, intensity of stirring, ionic strength, and in the case of reaction crystallization, the order and rate at which the reactants are mixed together. In addition, with respect to the kinetics and mechanics of the crystals, the shape will be influenced by:

• Different growth rates of the crystal faces
• Blockage and growth of certain faces due to the adsorption of impurities and additives
• Agglomeration\(^1\) of crystals
• Abrasion and attrition\(^2\) of crystals

Growth conditions can characterize the overall external impression or habit of crystals of the same substance in different ways. A distinction is made among prismatic, acicular, dendritic and plate-like crystals, or in the case of uniform growth in all spatial directions, isometric crystals. An elongated growth of the prismatic habit gives a needle-shaped crystal and a stunted growth gives a flat plate-like crystal. Excessively flattened crystals therefore, are usually called plates or flakes, an elongated growth in the vertical direction yields a needle or acicular crystal and flattened needle crystals are often called blades. Fig. 2.2 illustrates three different habits of a crystal belonging to the hexagonal system.

![Figure 2.2 Crystal habit on a hexagonal crystal](image)

Rapid crystallization from supercooled melts, supersaturated solutions and vapours often produces tree-like formations known as dendrites. Dendrites form most commonly during the early stages of crystallization. At later stages, a more normal uniform growth takes place.

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1. Agglomeration - The process of forming agglomerates - particles formed from smaller particles firmly cemented together by solid crystalline bridges.
2. Attrition - The reduction of particle size caused by crystal contacts resulting in small fragments breaking off.
and the pattern may be destroyed. Dendritic growth occurs quite readily in thin liquid layers while agitation tends to suppress this type of growth. Even if the crystals have a typical habit, they will not have an ideal lattice without defects. The higher the growth rate and the contents of foreign substances in the solutions, the larger the deviations from ideal crystals. Crystal defects can be subdivided into point defects (zero-dimensional), line defects (one-dimensional) and surface defects (two-dimensional). Point defects can be either empty spaces or spaces occupied by foreign units. Empty spaces or vacancies are important for the diffusion of substances in a crystalline lattice. Edge and screw dislocations are the two main types of line defect which can play an important role in the model of crystal growth. A variety of surface imperfections can be produced in crystalline materials as a result of mechanical or thermal stresses or irregular growth.

Most crystalline natural minerals and many crystals produced industrially, exhibit some form of aggregation or intergrowth. Aggregates refer to particles formed from smaller particles weakly held together. Aggregation is often indicative of impurity because crystal clusters readily retain impure mother liquor and resist efficient washing.

A composite crystal frequently encountered is known as a twin or a macle. It appears to be composed of two intergrown individuals, similar in form, joined symmetrically about an axis or a plane. Parallel growth and twinning are usually encountered when crystallization has taken place in undisturbed medium. Twinning occurs most frequently when crystals belong to the orthorhombic or monoclinic systems. Certain impurities in the crystallizing medium can cause twin formation even under vigorously agitated conditions. Fig. 2.3 illustrates the typical habits of gypsum from wet process phosphoric acid, including gypsum twins.

The formation of crystal clusters, aggregates or agglomerates, is probably more frequently encountered in large-scale crystallization than the formation of twins. Poor agitation, the presence of certain impurities in the crystallizing solution, seeding at high degrees of
supersaturation and the presence of too many seed crystals are among the factors that generally favour their formation. Small particles in liquid suspensions have a tendency to cluster together and in general, small crystals tend to agglomerate more easily than big ones.

### 2.2.5.1 Agglomeration

Unlike nucleation and growth, agglomeration is not a phenomenon occurring in all crystallization processes. The existence of agglomeration depends on the crystallizing system and on the crystallization conditions. It arises if crystals stick together to generate new, larger particles. Three types of agglomeration processes can be distinguished:

- If the cohesion forces are weak, the agglomeration is called flocculation.
- If the supersaturation sticks the agglomerating crystals strongly together, the process is called agglomeration.
- For processes arising without supersaturation, the process is called aggregation.

During crystallization processes, agglomeration is observed in the presence of supersaturation and aggregation is observed without supersaturation. To obtain agglomerates, three successive steps have to occur:

- Collision of two particles.
- Sufficient period during which the two particles stay together.
- Adherence of the two particles with the help of supersaturation.

The key parameters of this operation are thus:

- Hydrodynamic conditions such as mixing and local turbulence.
- Nature of the solvent (viscosity, density, etc.).
- Size and habit of the crystals.
- Population density of the crystals.
- Supersaturation and the related growth rate.
- Cohesion forces between the solvent, impurities and the crystals.

Agglomeration is a very important process during reaction crystallization (see Section 2.2.8) since the particles are generally very small and rather insoluble.
2.2.6 Crystal Habit Modification

Variation of the relative sizes of the faces of a particular crystal is called modification of habit. Rapid crystallization, such as that produced by the sudden cooling or seeding of a supersaturated solution, may result in the formation of needle crystals, impurities in the crystallizing solution can stunt the growth of a crystal in certain directions, and crystallization from solutions of the given substance in different solvents generally results in a change of habit. The degree of supersaturation or supercooling of a solution or melt often exerts a considerable influence on the crystal habit, as can the state of agitation of the system.

Habit modification is of the utmost importance in industrial crystallization. In almost every industrial crystallization process, some form of habit modification procedure is necessary to control the type of crystal produced. This may be done by controlling the rate of crystallization, the degree of supersaturation or the temperature, by choosing a particular solvent, adjusting the solution pH, deliberately adding an impurity that acts as a habit modifier, or even removing or deactivating some impurity that already exists in the solution.

The habit modifiers are either surface-active agents that adhere to specific crystal surfaces and retard their growth rate and result in a change of crystal habit, or are tailor-made additives. The shape and purity of crystals are influenced by impurities which alter the kinetic parameters as the rates of nucleation and growth. In some cases, a combination of the above methods may have to be applied.

Theoretically, there is no limit to a product crystal size but generally, there is a practical limit. Some crystals do not normally grow beyond a certain size in agitated industrial crystallizers. Some crystals have such low growth rates that excessive residence times would be necessary to produce large crystals. Increased residence time alone in an agitated crystallizer may not greatly influence the product size because of the inevitable occurrence of secondary nucleation which greatly increases the number of product crystals and consequently inhibits the development of large crystals. In some cases, crystals appear to become prone to attrition once they have grown beyond a certain critical size. To an extent, this can be attributed to increased damage from the agitator as higher rotational speeds are needed to keep them in suspension.
2.2.7 Control of Crystallization Processes

In order to meet the production objectives, all the variables affecting the crystallization process must be controlled within an acceptable range that is dictated by the chemical nature of the product, solvent and impurities present. Control of crystallization processes is through the desired properties of the final crystal product. Some of these properties are: narrow crystal size distribution, maximum crystal purity, high yield and acceptable crystal morphology. Depending on the type of product, one specification may be critical. A narrow crystal size distribution is always required but the desirable mean crystal size varies depending on the type of product. Well-formed crystals with uniform morphology that result in hard crystals, not susceptible to breakage are recommended.

In general, the morphology will be affected by the conditions of crystallization, crystal growth rate, purity of solution from which the crystals are formed, temperature, choice of solvent and concentration of the slurry. By altering one or more of these parameters, the morphology may be changed. Therefore, control over crystal morphology is a very complex process. It can be achieved by either a controlled growth rate through proper adjustment of supersaturation or by the addition of certain habit modifiers.

Irrespective of the mechanism of generation of supersaturation, impurities influence crystallization kinetics, crystal purity, crystal morphology and aggregation rate. The presence of even minute amounts of impurities substantially affects the kinetics of crystal nucleation, growth and dissolution. Crystal properties are also affected by the intensity of mixing, heat losses from the crystallizer, variations in the crystallizer head pressure and feed temperature and composition.

2.2.8 Reaction Crystallization / Precipitation

The crystallization mechanism of concern in this project is reaction crystallization (also known as precipitation). In this case, the supersaturation which is necessary for obtaining the crystallization, does not result from an action on the physical properties of the solution, but is obtained by a chemical reaction between two components. The solids generated are crystalline. Both the reaction and crystallization steps may be treated as occurring in series.
The study of reaction crystallization is more difficult than classical crystallization by temperature and/or concentration variations, because the crystals formed depend on different processes which all have their own kinetics (e.g. chemical reaction, crystallization and mixing). The competition among these three steps results generally in rapid crystallization, especially nucleation, which is very problematic to maintain under control, and in zones in the apparatus with different mixing conditions and, as a consequence, very different crystallization and reaction conditions. Control of the supersaturation in a precipitation process is difficult because it involves control of the mixing of reactants and the reaction rate. Precipitation does not depend on the presence of solute crystalline matter and therefore does not involve secondary nucleation. It results from homogeneous or heterogeneous nucleation processes (i.e. primary nucleation). Precipitation processes are generally initiated at high supersaturation, resulting in fast nucleation and the consequent creation of large numbers of very small primary crystals. Precipitation also includes the period of nucleus growth that takes place immediately after the nucleation event. Nucleation does not continue in this period because it is dependent on the relatively high levels of supersaturation that typically exist only during and immediately after the chemical reaction or rapid mixing of chemical reagents. Most depletion of supersaturation occurs because of the growth of nuclei which occurs in the final period of precipitation.

Precipitation can be greatly influenced by even minute amounts of admixtures present in the system. In addition to the kinetics of nucleation and growth, the particle shape, size and degree of agglomeration, as well as crystal modification or chemical composition of the precipitated compound may be influenced by admixtures. The presence of admixtures may also affect the bulk density and change the characteristics of filtration and of washing the filter cake.

Admixtures affecting precipitation processes can be divided into two broad categories. The first group includes those admixtures which are built into the crystal lattice of the solid being formed during precipitation and are the source of deformation to, and disturbance of, the lattice. The second group of admixtures are adsorbed on the crystal surface, particularly in the active sites or along the growth steps, therefore disrupting further growth.
From the physical viewpoint, a precipitated solid is characterized above all by the size and morphology of the particles.

2.2.8.1 Influence of Mixing

The crystallization of both soluble and slightly soluble substances is influenced by stirring. In the case of slightly soluble substances, with increasing stirring intensity, the induction period decreases, the number of particles being formed increases and, in some cases, the crystal growth rate also increases (as for example with CaSO\textsubscript{4}.2H\textsubscript{2}O - Smith and Sweett, 1971; Sohnel, 1981a; Sohnel and Handlirova, 1984a).

The morphology of the particles being formed is also dependent on the manner and intensity of stirring. During spontaneous precipitation under stirred conditions, small crystals having regular shapes are produced while in unstirred solutions, at the same initial supersaturation, dendrites and twin crystals are often formed, with size one or two orders of magnitude larger (Sohnel and Garside, 1992).

Detailed studies of the influence of stirring on precipitation have revealed that the precipitation rate, average size of particles being formed and the width of the size distribution all depend on the manner and rate at which the reacting solutions are mixed together (Turnbull, 1953; O’Hern and Rush, 1963; Kuboi et al., 1986; Mohanty et al., 1988).

The faster the solutions are thoroughly mixed, the higher is the precipitation rate, the smaller the average particle size and the narrower the crystal size distribution. The method by which solutions of reacting components are mixed and the intensity of their stirring can influence the progress of the precipitation and the physical characteristics of the product.

When precipitation results from mixing two separate reacting solutions, a number of processes must be taken into account, i.e. mixing of the reacting solutions, formation of the precipitated substance by a chemical reaction between the components, nucleation of the solid phase and growth of the particles formed.

In a precipitator, even if it is well mixed, three zones have to be differentiated:
• A zone near the reactant feed point. In the case of a fast chemical reaction leading to supersaturation, this zone will be more supersaturated than the average volume of the vessel; primary nucleation will occur at a high rate in this area.

• A zone near the stirrer in which the energy dissipation is much higher than in the average volume of the vessel. Breaking, agglomeration, secondary nucleation, or diffusion-controlled growth will be influenced.

• A zone comprising the average volume of the vessel.

Mixing of two liquids takes place in three stages:

• One liquid is dispersed in another so as to achieve a uniform average composition. On the microscale however, the mixture consists of entirely segregated parts of the two liquids and therefore, the local concentration differences correspond to the difference of concentrations of the non-mixed liquids.

• The size of the segregated regions of uniform composition increases and the contact area between the regions of different composition grows.

• Mixing by molecular diffusion occurs to such an extent that the segregated areas of uniform but mutually different composition disappear; the mixture attains complete homogenity on the molecular level.

The first of these three stages represents macromixing while the other two stages are called micromixing.

2.2.8.1.1 Macromixing

Macromixing can be defined as all the processes contributing to the uniformity of the local average value of the concentrations of all the species present in the vessel. Description of the macromixing state of an agitated vessel can be obtained with the assistance of the formulation of residence time distribution. A molecule or group of molecules called an aggregate can be characterized by the time between entering and exiting from the reactor, called its residence time.

Two macromixing limit states can be obtained for a given apparatus:

• The perfect macromixing for which the probability of exit for each molecule is the same at each point of the vessel. The average concentrations at each point are uniform and equal to those at the exit of the vessel.
The minimal macromixing for which the fluid is characterized by a unique residence time equal to the ratio of the volume of the reactor to the volumetric flow rate that is passing through it.

The modelling of a real precipitator needs an intermediate between these two extremes which has to be established for each apparatus.

In the initial seconds of the precipitation and the micromixing process in batch or semi-batch reactors, the two factors likely to affect mixing conditions are the feed point location and the stirrer speed. While only the primary nucleation is affected by the feed point location, the rates of primary nucleation, secondary nucleation, diffusional growth and agglomeration increase with stirring intensity.

**2.2.8.1.2 Micromixing**

The mixing phenomena at the molecular level called micromixing and depending on local energy dissipation, also have to be taken into account since they are well known to influence fast non-linear kinetics very dramatically. Primary nucleation is a good example of such a rapid non-linear phenomenon at high supersaturations, particularly near the feed point of reactants with a fast chemical reaction.

**2.2.8.2 Secondary Changes of the Precipitated Phase**

Although precipitation, like all crystallization processes, consists of three basic steps (supersaturation, nucleation and growth), subsequent secondary processes can cause further changes of the physical and chemical properties of the precipitated phase during contact with the mother liquor. These processes are recrystallization, ripening, ageing, aggregation, agglomeration and coagulation and these can cause major changes in the precipitate size distribution and the final crystalline product.

The following definitions (Nyvlt et al., 1985) explain the above concepts:

*Recrystallization:* a process which involves the change of size, and/or the shape of crystals by the mechanism of surface diffusion of the solid or mass transfer through the liquid phase.
Depending on the conditions, isothermal (known as Ostwald ripening) and non-isothermal recrystallization can be distinguished.

**Ripening (also isothermal recrystallization or Ostwald ripening):** often a fast process resulting in a shift of the crystal size distribution towards larger sizes under isothermal conditions as a result of the larger crystals growing at the expense of the smaller crystals which gradually dissolve and eventually completely disappear.

**Non-Isothermal Recrystallization:** a process occurring during temperature or concentration fluctuations with an effect similar to ripening, but occurring at much larger particles than for Ostwald ripening.

**Ageing:** usually a slow process causing microscopic or even macroscopic changes in the solid phase, especially changes of the crystal modification, habit, specific surface or chemical composition of the solid phase.

**Aggregation:** clustering of separate particles to form larger particles, held together weakly.

**Agglomeration:** clustering of the primarily formed crystals into more stable secondary particles held together mainly by crystalline bridges and sometimes by physical forces.

**Coagulation:** a particular case of agglomeration occurring only for very small particles where the clusters are held together solely by physical forces.

### 2.2.8.3 Modifying Crystal Size Distributions

The primary crystal size distribution obtained just after precipitation has ceased is often very different from that in the final product. The original crystal size distribution can be modified considerably by secondary changes in the suspension prior to solid separation.

#### 2.2.8.3.1 Batch Precipitation

Precipitate size distribution and crystal morphology are determined by the interplay between nucleation and crystal growth. A narrow size distribution will be obtained if nucleation is initially rapid but then stopped abruptly and growth allowed to take place on the resulting crystals without particle agglomeration. The shape of all the crystals is also likely to be similar, the shape often depending on the supersaturation at which growth occurred. At low
growth supersaturation, the crystals develop a near-equilibrium shape while high
supersaturations favour the preferential growth of certain crystal faces. If nucleation and
growth proceed simultaneously, the resulting crystal size distribution is wide and a variety of
crystal shapes are formed.

Batch precipitation is usually carried out by adding a solution of one reactant to a second
reactant solution that is already present in a vessel. Local variations in supersaturation due to
both macro- and micromixing are expected (see Section 2.2.8.1). Mixing therefore exerts a
considerable influence on the course of precipitation and on the crystal size distribution of the
precipitate. In general, the better the mixing, the higher the average supersaturation and thus
the higher the nucleation rate. The higher nucleation rate lowers the average crystal size and
therefore, increasing the mixing intensity usually decreases the final crystal size.

A decrease in supersaturation can sometimes be achieved by increasing the reaction
temperature provided that the solubility of the precipitating compound increases significantly
with temperature. However, the increased temperature also enhances the nucleation and
growth rates and therefore, prediction of the influence of temperature for a particular system
is difficult.

The feed point location is important if stirring is inadequate. The feed rate may also be
important if seeds are added prior to precipitation.

2.2.8.3.2 Semi-Batch Precipitation

In general, semi-batch precipitation yields larger crystals than batch precipitation of the same
system. Larger crystals can usually be obtained when the concentration of reactant solutions
is reduced. Depending on the particular system, a decrease of the feed rate may either result
in little effect on the crystal size distribution, or may promote formation of larger crystals.
Locating the feed points far apart and in turbulent regions of the tank result in increased
crystal size since excessive nucleation around the feed points is eliminated. Increasing the
stirring rate can either increase or decrease the crystal size, depending on the particular
system and on the actual hydrodynamic conditions prevailing in the reactor. A limiting
stirring intensity may exist, above which no further influence on the crystal size distribution is observed.

2.2.8.3.3 Continuous Precipitation

A narrow crystal size distribution can be expected when conditions during continuous precipitation approximate to plug flow. A wide crystal size distribution is always obtained from an ideal mixed suspension, mixed product removal precipitation. Deviations from mixed suspension, mixed product removal conditions, are usually far more effective in influencing precipitator performance than are kinetics. Therefore, factors such as mixing, residence time distribution of the solid and liquid phases and the position of the feed point are important. For unpremixed feeds, an increase of both mixing intensity and residence time leads to an increase in the precipitate crystal size. If premixed solutions are fed to a reactor, increase in the mixing intensity and decrease in the reactant solution concentrations increase the particle size, but the particles are generally smaller than in the unpremixed feed case.

2.3 Gypsum Crystallization Literature

2.3.1 Introduction

Gypsum, CaSO$_4$.2H$_2$O, known as dihydrate, is the most useful form of calcium sulphate, CaSO$_4$. It is useful as an industrial material because it loses its water of hydration when heated, producing partially or totally de-hydrated calcined gypsum. When water is added to this calcined gypsum, it reverts to the original dihydrate. The dehydration of gypsum, commonly referred to as calcination in the gypsum industry, is used to prepare hemihydrate, CaSO$_4$.½H$_2$O, or anhydrite, CaSO$_4$. A controlled, modest amount of heat converts gypsum to hemihydrate.

The CaSO$_4$.H$_2$O system is characterized by five solid phases. Four exist at room temperature: calcium sulphate dihydrate, calcium sulphate hemihydrate, anhydrite III and anhydrite II. The fifth phase, anhydrite I, only exists above 1180°C. The physical characteristics of the known phases of calcium sulphate have a diverse nature as indicated by
their widely varying crystal modification, aggregation state and internal structure. Each calcium sulphate phase could exist in several forms with widely varying physical characteristics, depending on the manufacturing process.

The hemihydrate may be manufactured in three different forms, including α-hemihydrate, β-hemihydrate, and aged β-hemihydrate, each with a characteristic crystalline structure, surface area, and porosity. They differ from each other in their application characteristics, their heats of hydration and their methods of preparation. The α-hemihydrate consists of compact, well-formed, transparent, large primary crystals. The β-hemihydrate forms flaky, rugged secondary particles made up of extremely small crystals. The interaction of the compounds with the environmental conditions such as adsorption of water and heat transfer, depends on the character of the surface and the magnitude of the area.

The crystal structure of calcium sulphate consists of chains of alternate Ca\(^{2+}\) and tetrahedral SO\(_4^{2-}\) ions. In calcium sulphate dihydrate, the water of crystallization is embedded in between the layers, forming a layer lattice and thus allowing easy cleavage along these planes. When calcium sulphate is dehydrated from dihydrate to hemihydrate, the volume decreases, and wide channels that run parallel to the CaSO\(_4\) chain are formed. The water of crystallization is loosely bound in definite positions in these channels, hence the water is able to escape relatively easily, explaining the easy conversion to anhydrite III. Anhydrite II exhibits the closest packing of ions which makes it the densest and strongest of the calcium sulphates. However, it reacts very slowly with water.

Mineral calcium sulphate is commonly called anhydrite and occurs in many parts of the world. The mineral gypsum, calcium sulphate dihydrate is widely distributed and is of much more economic importance. The various gypsum and anhydrite deposits differ in purity, structure and colour.

There are two types of gypsum: a natural mineral and a synthetic product of chemical reaction from a variety of industries. Natural gypsum is seldom found in the pure form. Flue-gas gypsum is obtained from the desulphurization of combustion gases of fossil fuels in large combustion plants, especially power stations. The largest amount of by-product gypsum is obtained from the production of wet phosphoric acid from phosphate rock and
sulphuric acid. Calcium sulphate dihydrate is also formed in the production or treatment of organic acids (e.g. citric acid, tartaric acid and oxalic acid) or inorganic acids (e.g. boric acid). All of these acids are produced by reaction of their calcium salt with sulphuric acid. Calcium sulphate dihydrate shows different drying behaviour for natural gypsum and gypsum obtained by hydration of hemihydrate. The compounds with a higher state of hydration have a tendency to lose higher amounts of water when exposed to conditions of low humidity, even at room temperature. In an industrial environment where the product is often a mixture of several calcium sulphate phases, it makes the design of the drying procedure for such material difficult.

2.3.2 Influence of Impurities

The final physical form of gypsum is of critical importance since these are the properties that affect downstream processing. In industrial practice, gypsum normally crystallizes in the presence of many different impurities, some of which can exert a considerable influence on the precipitation process. The influence of specific impurities on the degree of agglomeration is therefore important. Nucleation and growth kinetics can both be strongly affected by the presence of trace impurities, as can the crystal shape and morphology. It must be noted also, that gypsum crystals growing in agitated suspensions have a tendency to form agglomerates.

A number of references relating to the influence of additives and impurities on the crystal size and habit were sourced. Much of this literature provided a useful base to approaching laboratory scale work (see Chapter 6).

Budz et al. (1986) investigated the precipitation of gypsum in a laboratory-scale Continuous Mixed Suspension Mixed Product Removal (MSMPR) Crystallizer under carefully controlled conditions. Precipitation was first studied in pure brine solutions and then the actions of three additives on habit modification were observed. The first additive used was Al\textsuperscript{3+}, added as AlCl\textsubscript{3}, since this impurity is often encountered in industrial processes using natural ore feedstocks where gypsum is formed as a by-product. The other additives used were the di-sodium salts of fumaric and maleic acids. These additives were used to investigate the claim
of Tadros and Mayer (1979) that gypsum crystals grown in the presence of maleate ions are habit modified, while fumarate ions, have no influence.

The 250 cm³ mixed suspension, mixed product removal crystallizer was operated at 20°C with an agitator speed of 720 rpm. The crystallizer was fed at identical flowrates, with two undersaturated equimolar reagent solutions prepared from deionised water, reagent-grade CaCl₂·2H₂O and anhydrous Na₂SO₄. These solutions reacted to form a supersaturated solution of gypsum. The feedrates were maintained to give crystal and liquor residence times in the range of 10-60 minutes and the initial gypsum concentration was varied over a low range (0.032 - 0.075M). The ranges of additive concentration used were 10-200 ppm (mg impurity/kg solution) for Al³⁺, 120-800 ppm for maleate ions, 120-300 ppm for fumarate ions.

Histograms from a Malvern particle sizer indicated that there were two independent distributions in the suspension, i.e. agglomerates and discrete crystals. In pure brine, only the smallest crystals, up to about 5μm, remained discrete. Al³⁺ addition produced a marked increase in the degree of agglomeration: no single crystals were seen. In the presence of fumarate and maleate ions, agglomeration was also observed. In the presence of aluminium ions the agglomerates exhibited a more open structure in comparison with those from pure brine solution, whereas maleate ions appeared to induce the opposite effect.

The influence of the additives on crystal habit was also reported. The gypsum crystals precipitated from pure brine were found to be elongated. The presence of aluminium ions caused the gypsum crystals to increase in size and be more plate-like than those from pure solutions. Maleate ions were found to promote the development of rod-shaped crystals. The presence of fumarate ions resulted in more elongated crystals, including some star-like agglomerates.

Runs with the same initial concentration (0.0375M) using pure solutions and solutions with impurities, facilitated qualitative estimates of the crystallization rate from the dependence of supersaturation on residence time. For a given residence time, the presence of Al³⁺ resulted in a much higher supersaturation level being established. This behaviour would be expected if there were a retardation of either nucleation or growth. Similar behaviour was found for
maleate ions and, to a lesser extent for fumarate ions. Runs using higher concentrations of the additives (183 and 800 ppm respectively), resulted in total inhibition of crystallisation, providing further evidence of gypsum growth retardation by Al\(^{3+}\) and maleate ions.

Sarig and Mullin (1982) examined the effect of Al\(^{3+}\) and F\(^{-}\) ions on the precipitation of calcium sulphate, under carefully controlled laboratory conditions, with particular focus on the pre-embryo stage of nucleation. The technique involved the detection of rapid conductivity changes in a supersaturated solution as it nucleated.

Gypsum was precipitated in a stopped-flow cell by mixing equimolar solutions of CaCl\(_2\) and Na\(_2\)SO\(_4\) in the concentration range 0.05-1M. Two feedstock concentrations were used: 0.05M and 0.25M which gave gypsum supersaturation levels of S~1.2 and S~6 respectively.

The first trace additive used, AIF\(_3\), was added to the Na\(_2\)SO\(_4\) reactant solution. The effects of various concentrations of AIF\(_3\) on the induction periods for CaSO\(_4\) precipitations were recorded. For precipitation of 0.05M-CaSO\(_4\), the induction periods were found to increase with aluminium concentration up to 0.42% Al\(^{3+}\) (on a mass basis related to the amount of CaSO\(_4\) created in solution), but to decrease again for the higher value of 0.64%.

Scanning electron microscope (SEM) micrographs (x 1600) were taken of the gypsum crystals precipitated in three of the 0.25M series of runs. Irregular thin plates and rods were precipitated from the pure system. Some well developed plates appeared along with finely shaped needles in the presence of 0.04% Al\(^{3+}\) and 0.085% F\(^{-}\). Small irregular particles were evident on the surfaces of the crystals precipitated in the presence of 0.24% Al\(^{3+}\) and 0.51% F\(^{-}\). Due to the appearance of small particles on the surfaces of the gypsum crystals, the effects of Al\(^{3+}\) and F\(^{-}\) addition were investigated separately.

For the Al\(^{3+}\) series, the trace additive used was AlCl\(_3\). The gypsum precipitated in the presence of 0.2% Al\(^{3+}\) in the form of substantial rods and granular crystals. The clear absence of small particles on the surfaces of the crystals, in contrast with those seen for precipitation in the presence of 0.24% Al\(^{3+}\) added as AIF\(_3\), suggested that these particles might have been induced by the presence of fluoride.
For the F− series, KF was added. The crystals which precipitated in the presence of more than 0.25% F− exhibited deposition of small particles of 'foreign' matter onto the crystal surfaces. These particles were thought to be CaF$_2$.

This investigation showed that both Al$^{3+}$ and F$^−$ ions affected the formation of gypsum during the first few milliseconds of precipitation, i.e. during the early stages of growth and probably at the initial stage of nucleation. Al$^{3+}$ ions exist in aqueous solutions as aquo-complexes [Al(H$_2$O)$_6$]$^{3+}$ and these species could adsorb on gypsum nuclei soon after their formation, blocking growth sites, retarding precipitation and slightly prolonging the induction period. When fluoride is also present, the action may be through the adsorption of an aluminium fluoride complex.

The retarding effect of aluminium on the induction period was expected to become more pronounced, the higher the concentration of aluminium aquo-complexes in the solution. For precipitation from the 0.05M reactant solution, the induction period was found to increase until the Al$^{3+}$ ion concentration reached 0.42%, but to decrease at higher impurity concentrations. For the 0.25M reactant solution, the induction period increased until the Al$^{3+}$ ion concentration reached 0.1% and decreased at higher impurity concentrations.

Several observations were made in connection with this study. The concentration of individual complex molecules of [Al(H$_2$O)$_6$]$^{3+}$ was found to be primarily dependent on Al$^{3+}$ ion concentration, pH and the availability of free water in the system. In relatively concentrated Al$^{3+}$ solutions, the concentration of free water was low and deaquation of the aquo-complexes led to the formation of polynuclear complexes. The concentrations of Al$^{3+}$ used in the study (0.64% and 0.2% in 0.05M and 0.25M-reactant solutions respectively) were too low to induce the formation of polynuclear complexes in pure aqueous solutions. However, the solutions used were supersaturated with respect to gypsum and contained high concentrations of strongly solvated Ca$^{2+}$ and consequently had relatively low free-water concentration. The [Al(H$_2$O)$_6$]$^{3+}$ species which are most probably responsible for the poisoning of growth sites in gypsum and the consequent retardation of growth rate, exist in equilibrium only with the free water in a system.
Sarig et al. (1981) assessed the influence of aluminium and silica ions on the shape, average size and size differences of calcium sulphate dihydrate crystals formed in pure aqueous solutions. Calcium sulphate was precipitated from Na$_2$SO$_4$ and CaCl$_2$ solutions (0.18-0.25M) in a steady state crystallization system. The additives used were Al$_2$(SO$_4$)$_3$.18H$_2$O and silica from sodium silicate solution (water glass, 50% SiO$_2$). The residence times were in the range of 19-58 minutes.

The gypsum crystals produced before the attainment of steady state were in the form of irregular plates with a significant fraction of them twinned. At steady state in a 0.2M solution, the gypsum crystal population consisted of separate very thin needles, broader rods and elongated plates.

Two sets of experiments were performed to determine the influence of fluctuations in concentration or operational conditions on the crystal characteristics. The first series included variation of the concentration with a constant residence time of 32 minutes. Slight fluctuations in concentration (0.18M and 0.25M solutions) appeared to have little effect on the shape and size distribution of the crystals. The second series of experiments involved increasing the residence time while holding the concentration constant at 0.2M. A residence time of 58 minutes yielded crystals significantly larger than those formed at a residence time of 32 minutes. At a residence time of 19 minutes, the crystals were found to be agglomerates of very small crystallites which were evidently twinned.

It was found that the addition of aluminium ions had a strong beneficial effect on the characteristics of gypsum crystals, i.e. on their filterability and washability. The appearance of the crystals grown with the addition of 0.5% Al$^{3+}$ confirmed the significant effect on the gypsum crystals. The change of behaviour was the result of change of crystal habit and size distribution. The more pronounced the needle-like habit, the smaller the average size and the wider the size distribution. Hence the poorer the filterability and washability. On the other hand, crystals grown in the presence of silica ions were very small and thin, forming hedgehog-like agglomerates.

At low concentrations, aluminium ions exist mostly as hexaaquo complexes (Aveston, 1965). Due to a high charge, they tend to adsorb on crystal faces, retard growth, and prevent their
development on surfaces of newly formed nuclei. These activities cause the formation of a low number of relatively large crystals. Silica ions appear as polymeric species which are not easily soluble in aqueous solutions at nearly neutral pH. Such polymers serve as ready heterogeneous nucleation centres, interfering with the normal secondary nucleation process characteristic of steady state systems with a high fraction of solid material in suspension. This nucleation sequence gave rise to a profusion of crystals and as the available solute was limited, the individual crystals were very small.

Weijnen and Rosmalen (1984) investigated the influence of various additives and impurities, relevant to industrial practice, on the crystallization process of gypsum. Four commercially available inhibitors, one bisphosphonate and three polyelectrolytes, were used for this study. As a phosphonate inhibitor, 1-hydroxy-ethylidene-1, 1-bisphosphonic acid (HEDP) was used. The polyelectrolytes used were Belclene 200, Belclene 283 and Belsperse 161, all polycarboxylates. Various growth and nucleation experiments were carried out to compare the inhibitor effectiveness of the three polyelectrolytes and HEDP. It was found that all the inhibitors promoted the development of relatively short and thick gypsum crystals while plate-like crystals were formed in the absence of inhibitors. No evidence was found that the inhibitors stimulated agglomeration of the growing seed crystals. The habit modifying influence of HEDP was found to increase with increasing HEDP concentration and pH value. When nucleation occurred in the presence of HEDP, the inhibitor was found to stimulate abundant agglomeration in spite of its dispersive properties. This phenomenon was more pronounced as HEDP concentration and the level of supersaturation were raised. For inhibitors of the polyelectrolyte type, a similar agglomerating and habit modifying influence was found during the nucleation and growth of gypsum crystals.
2.3.3 Gypsum Crystallization - Phosphoric Acid Process

Most of the available literature concerning the production of gypsum crystals, refers to the gypsum produced as a by-product of the phosphoric acid process.

The “wet process” method of producing phosphoric acid consists of reacting phosphate rock (calcium phosphate) with sulphuric acid, in an environment containing reaction product phosphoric acid and reaction product gypsum, according to the general chemical equation:

\[ 3\text{H}_2\text{SO}_4 + \text{Ca}_3(\text{PO}_4)_2 + 6\text{H}_2\text{O} \rightarrow 2\text{H}_3\text{PO}_4 + 3\text{CaSO}_4 \cdot 2\text{H}_2\text{O} \]

The crystallization of gypsum is the most important operation in the production of phosphoric acid by acidulation of phosphate rock with sulphuric acid. It is necessary to remove the gypsum from the acid in order that the phosphoric acid may be used in subsequent reactions. The most common method of gypsum removal is by filtration. Some of the filtration difficulties encountered include low filtration efficiency and inefficient separation of the phosphoric acid from the gypsum. Therefore much larger filtration surfaces for a given size plant are required and a relatively large fraction of the phosphoric acid product remains entrapped in the gypsum cake. Hence, the filterability of gypsum crystals has major effects on the overall process efficiency. The ease with which the gypsum can be removed from the phosphoric acid depends on the physical conditions of the gypsum, that is, the shape, size and size distribution of the gypsum crystals.

The formation of gypsum crystals of the required shape and size results in greater filtration efficiency both by improving the filtration rate and by reducing \( \text{P}_2\text{O}_5 \) losses in the cake. In addition, some economy in pumping costs may also be achieved due to lowering of the phosphoric acid-gypsum slurry viscosity. The formation of crystals with a low length to width (L/W) ratio and a narrow size distribution, in addition to a shape closer to hexagonal, was shown to result in lower viscosity pulps, higher filter permeability and therefore, greater filtration efficiency (Cocheci and Rosca, 1982).

For optimum filtration and washing, equant crystals of uniform size are most desirable. As the range of crystal sizes increases, the cake tends to become less permeable. Permeability of
the cake is also affected by crystal shape. Plate-like crystals give a highly impervious cake while prismatic crystals may produce a cake having excessive void space. Extremes of shape also tend to render the crystals more fragile, resulting in the formation of fine fragments by attrition. In the case of phosphate gypsum, thick rhombic crystals or agglomerates appear to give better filtration characteristics than thin plates or needles. Therefore, any process variables which tend to affect the crystal size and habit are important.

One of the most important factors affecting the crystal size is the number of crystals growing, which in turn depends on the number of nuclei formed in the crystallizer. The rate of nucleus formation is a function of supersaturation and because the solubility of gypsum in phosphoric acid depends on P₂O₅ and H₂SO₄ concentrations, these are among the most important variables affecting crystal size. The size and shape of the gypsum crystals produced, also depends on factors such as temperature and the presence of impurities in the phosphate rock.

All of these factors affect the crystal properties in different ways and to various extents. The excess sulphate concentration has a more significant effect than other factors on crystal shape and produces crystals that are needle-shaped with poor filtration characteristics. Sulphate concentrations are typically in the range of 1.0 to 4.0%. Stars, consisting of needle-like crystals radiating from a central nucleus, usually indicate a high sulphate concentration.

At slightly lower sulphate concentrations, rather large individual rhomb-shaped gypsum crystals, with a length not exceeding two or three times the width are formed. At still slightly lower sulphate concentrations and within a rather narrow range, it is possible to grow agglomerates or twins. These consist of rather large crystals and up to about four are grown together on one or more face, with the major axes of the crystals apparently having random orientation. Low sulphate concentrations generally produce small crystals in the form of thin plates. These effects are due primarily to changes in the growth rate since sulphate concentration has a major effect on the solubility of CaSO₄, and thus on the degree of supersaturation at any constant P₂O₅ concentration. (Gilbert 1966).

In industrial practice, it is very difficult to produce crystals of consistent shape and size due to problems in controlling the multitude of factors affecting them. Therefore, it may be
necessary to add some external chemical reagent or additive which would result in enhanced filtration efficiency.

Several investigations have examined the effect of various chemical additives on the habit of both hemihydrate and dihydrate crystals of gypsum produced in the manufacture of phosphoric acid.

An invention by Leyshon et al. (1965) relating to improvements in the “wet process” method of manufacturing phosphoric acid so as to improve the filterability of the reaction product gypsum from the reaction product phosphoric acid, had the following objectives:

- to provide an improved process for producing phosphoric acid where the gypsum crystals produced could be readily filtered from the phosphoric acid,
- to produce gypsum crystals which could easily be washed with a minimum loss of soluble $\text{P}_2\text{O}_5$,
- to obtain maximum extraction of $\text{P}_2\text{O}_5$ from the phosphate rock,
- to use unground or calcined rock for the commercial production of phosphoric acid.

It was found that a substantial increase in the filtration rate of these normally difficult to filter gypsum slurries was attained if the reaction was carried out in the presence of a small amount of an additive of the alkyl aryl sulphonic acid type. The alkali metal salts of the acid were the preferred additives. The required amounts of the additives were found to be 0.1 to 2.0 lbs of alkyl benzene sulphonate acid or about 0.1 to 3.2 lbs of isopropyl naphthalene sulphonate acid per ton of phosphate rock. The preferred sulphonates were the sodium alkyl benzene sulphonate having an alkyl group of about 9 to 12 carbon atoms, and in particular the sodium decyl benzene sulphonates.

The faster filtration rate was due to the change in crystal structure which occurred. The chemical reaction by which the desired gypsum crystals were formed was explained by the addition of the additives which promoted the formation of many nuclei which grew in a direction opposite to the growth of elongated crystals from existing nuclei. This resulted in crystals with a smaller width to length ratio and a more hexagonal shape.
The improved invention resulted from the presence in the reaction mixture, at a time when the reaction was in progress and the gypsum crystals began to form, of a small amount of one of the additives above. The addition of the additives after the gypsum crystals were formed was found to be ineffective. In addition, the amount of additive required to improve the filterability characteristics of the gypsum fell within a specific critical range and when an overdose of the additive was used, the filtration rate was found to be worse than if no additive was used.

Although the critical range required to obtain the desired results varied with the type of phosphate rock used and the additive employed, it was determined that there was:

- a low limit at which no beneficial results were achieved,
- an optimum range where the filtration rate was at its maximum,
- an upper limit where again there was no improvement in the filtration rate,
- an amount beyond this upper limit where the addition of the additive was definitely harmful to the filtration rate.

Harmful effects included the formation of foam or froth which caused phosphoric acid to overflow out of the reaction equipment and into the fume and vacuum system. Excessive amounts of the additives also caused dispersion of any slimes or fine gypsum present, and permitted the passage of the slimes or fines through the filter into the product phosphoric acid.

Besides improved filtration, other advantages achieved by the improved process were lower cake moisture and complete elimination of cake cracks, as well as lower washing losses. The gypsum cakes obtained were 80-85% solids as compared to 75-78% solids from conventional good gypsum. A reduction of 0.5-1.0% in water soluble losses was achieved.

The addition of the additives was effective when unground or calcined rocks were used. In both of these cases, the rate of digestion of phosphate rock was slower than where ground uncalcined rock was used. Coarse rock tended to coat with precipitated gypsum, leaving a core of unreacted rock and making stoichiometric control of sulphuric acid addition difficult. In most instances, calcination tended to glaze or densify the phosphate rock making it more susceptible to gypsum coating and poor reaction control. Use of the additives, materially
aided in improving the digestion properties of the phosphate rock and also improved the gypsum formed from these rocks.

Rocha and Ciminelli, 1995 studied the effects of surfactants on the morphological and granulometric features of gypsum with the objective of improving filterability. Experiments were performed in both batch and continuous modes to investigate the effect of dodecylbenzenesulfonic acid (DBSH) and sodium diisoctilsulfosuccinate (SSNa) on the size and morphology of calcium sulphate.

Batch precipitation experiments were carried out in a 1000 ml stirred glass reactor immersed in a thermostatic bath. The reacting solutions were composed of 28% \( P_2O_5 \) and 0.8% CaO (solution A), along with 28% \( P_2O_5 \) and 15.2% \( H_2SO_4 \) (solution B). All solutions were prepared on a weight percent basis. Surfactants were added to solution A prior to the experiments. DBSH was tested in the 5 to 500\( \mu g/g \) range, and SSNa was tested in the 50 to 500\( \mu g/g \) range. Calcium sulphate seeds were used as precipitation nuclei and were added at a dosage of 6% of the final precipitate weight.

In the continuous experiments, solution C, containing 28% \( P_2O_5 \) and 20% \( H_2SO_4 \), and solution D, containing 28% \( P_2O_5 \) and 2.0% CaO, were fed to a 500 ml reactor at a constant flowrate. The trials were run for 10 hours at a constant temperature of 343K with a residence time of 1 hour and 50 minutes.

The DBSH was found to be an effective habit and size modifier in gypsum crystallization for concentrations up to 5\( \mu g/g \). At such concentrations, reductions in the length to width ratio were observed (order of 194% in the batch systems and 177% in the continuous systems). In the batch systems, at 10\( \mu g/g \), the DBSH totally suppressed gypsum formation, favouring the precipitation of hemihydrate crystals (aciculate crystals and sheaf-like clusters). Above 50\( \mu g/g \), this surfactant inhibited the formation of any solid product, even in the presence of precipitation nuclei and high supersaturation levels.

The addition of 200\( \mu g/g \) of SSNa resulted in a significant increase in the gypsum crystal size as well as a 21% and a 60% reduction in their length/width ratio in batch and continuous systems respectively.
Moudgil et al. (1988) examined the efficiency of gypsum filtration and its relation to the shape of the crystal formed as a function of both the sulphate ion concentration and polymer additives. The additives used to modify the crystal habit of dihydrate and hemihydrate gypsum were poly-1-glutamic acid and polyvinyl sulphonate. The effect of the polymers on the crystal habit of gypsum formed using natural phosphate rock (apatite) under highly acidic conditions (pH < 1) was studied. The performance of the additives was examined in terms of improvements in the filtration rate.

Partial dissolution of 80g of apatite was achieved by agitating the solids with 220 ml of 38.5% \( \text{H}_3\text{PO}_4 \) and 4 ml of 98% \( \text{H}_2\text{SO}_4 \) in a 500 ml flask for 24 hours at 72±5°C. Following the initial dissolution, the hot slurry was transferred to a 500 ml standard mixing vessel with a turbine impeller. 23-43 ml of 98% \( \text{H}_2\text{SO}_4 \) was added to the slurry to maintain a specific CaO to \( \text{SO}_4^{2-} \) ratio in the beginning, and crystallization was carried out for 6 hours at 72±2°C. The gypsum formed consisted of both hemihydrate and dihydrate crystals.

The results of the study indicated that a decrease in the \( \text{Ca}^{2+} /\text{SO}_4^{2-} \) ratio from 1.1 to 0.75 resulted in a significant increase (1.6 times) in the filtration rate while an increase in the ratio to 1.3 showed no noticeable change. The increase in filtration rate at high sulphate concentration was due to either changes in solution properties such as a lower viscosity, or due to filter cake characteristics. An evaluation of the effect of temperature on the viscosity of a 40% \( \text{H}_3\text{PO}_4 \) solution, indicated that changes in viscosity alone could not account for the improvement in the filtration rate. Also, no significant change in the viscosity was observed as a function of sulphate concentration. These observations suggested that an increase in the filtration rate at high sulphate concentration was mostly due to changes in the cake parameters. Examination of the crystal shape showed that a high sulphate concentration produced thin lozenges while a higher calcium content resulted in needle shaped crystals.

Polyglutamic acid did not dissolve in water at neutral pH values even at very low concentrations (50 ppm). When the pH was increased to approximately 10, a clear solution resulted and when the pH was reduced to less than 1, no precipitation was observed. Addition of the polyglutamic acid from a high pH stock solution resulted in a 42% increase in the filtration rate. An increase in the concentration of the additive to 38 ppm did not show
any significant change in the filtration rate, however, an increase in the molecular weight did result in a lower filtration rate.

Enhanced filtration rates were obtained with both additives. Increases of 50 and 32% in the filtration rate resulted from the addition of poly-1-glutamic acid and polyvinyl sulphonate respectively. The improvement in the rates were found to be directly related to the aspect ratio of the crystals formed, however, this correlation could not be generalised and may be specific to the cake formed in the study.

The viscosity of the phosphoric acid product was found to increase by 6% in the presence of poly-1-glutamic acid, which had an adverse influence on the filtration rate. However, even with the negative effect on the filtration rate, the addition of poly-1-glutamic acid resulted in enhanced filtration.

*In wet process phosphoric acid production, a difficulty arises due to the presence of small but significant amounts of impurities in the phosphate rock, such as Fe$^{3+}$, Al$^{3+}$, Mg$^{2+}$, silicofluorides and organic matter. These impurities can have large effects on the filterability of the gypsum crystals produced in the process, reducing the filtration capacity by a factor of as much as 4.*

Adami and Ridge (1968) studied the properties of gypsum formed by hydration of the hemihydrate in a medium containing 29.4% P$_2$O$_5$ at the end of the reaction. Hydration of calcium sulphate hemihydrate was carried out in a glass vessel fitted with a stirrer and immersed in a temperature-controlled water bath. Satisfactory conditions [i.e. conditions relative to the formation of chemical gypsum but not leading to the formation of orthorhombic calcium sulphate (anhydrite)] were provided by a system with a solids to liquid ratio of 1:5 and containing 29.4% P$_2$O$_5$ and 5.6% H$_2$SO$_4$ when hydration was complete. The small amount of sulphuric acid was added to simulate the effect of residual acid at the end of digestion. In some experiments, 2% each of Al$_2$O$_3$ (as the sulphate), Fe$_2$O$_3$ (as iron (III) chloride) and HF were added because fluorides and compounds of iron and aluminium commonly occur in rock phosphate.
Hydration was found to be slow below 35°C. At temperatures above 60°C, the formation of orthorhombic calcium sulphate was significant. This was in the form of small grains (approximately 5 μm wide) which caused filtration difficulties. The dihydrate was formed in the range 35-60°C and variations in the temperature were found to have little effect on the habit.

The addition of 2% each of Al₂O₃, Fe₂O₃ and HF to dry calcined material resulted in a change from highly acicular crystals (about 500 μm long and 30 μm wide) in the absence of the additives, to equi-axial grains (about 200 x 100 μm in dimension) with crystallographic faces. The addition of these additives therefore resulted in the crystallization of good filtration quality equi-axial grains.

The effect of temperature on the composition of calcium sulphate dihydrate formed in media containing 29.4% P₂O₅, both with and without the addition of 2% each of Al₂O₃, Fe₂O₃ and HF was also investigated. The phosphate content fell to virtually zero as the temperature rose from 52.2 to 57.5°C. In the absence of the additives, the aluminium content of the phosphate-free sulphate was 0.25% as Al₂O₃. For the same type of material prepared in the presence of the additives, the contents were:

- Al₂O₃, 0.2%
- fluoride as CaF₂, 0.1%
- chloride as NaCl, 0.02%.

The pH of all the samples was between 3.5 and 4.5. The amounts of iron and aluminium found in the precipitated dihydrate were, if anything, less than in the original hemihydrate, even when considerable amounts of iron and aluminium were added to the system. The amounts of fluoride found were also quite small.

Research by Hasson et al. (1990) investigated the effect of a single impurity, either Fe³⁺ or Al³⁺, on calcium sulphate crystallizing in pure phosphoric acid solution. The effect of impurity concentration on both crystal size distribution and filter cake specific resistance was studied.
Chapter Two - Literature Review

Two feeds consisting of an acidified calcium phosphate solution and a sulphuric acid solution were fed to a vessel which acted as a reactor and as a mixed suspension, mixed product removal crystallizer. A reaction volume of 580 cm$^3$ was maintained by use of an overflow mechanism. These reacting streams caused crystallization of gypsum. The impurity was added with the sulphuric acid feed. Ferric ion impurity was obtained by dissolving Fe$_2$(SO$_4$)$_3$.7H$_2$O in the sulphuric acid feed solution. Similarly, aluminium impurity was obtained by dissolving Al$_2$(SO$_4$)$_3$.16H$_2$O in the sulphuric acid feed. All runs were carried out under identical conditions in the reaction-crystallization volume:

- residence time = 24 minutes
- temperature = 40°C
- phosphoric acid concentration = 38.5 wt.% P$_2$O$_5$
- gypsum slurry concentration = 4.7 wt.% (70 g/litre filtrate).

The Fe$^{3+}$ impurity content was varied from 0 to 0.35 mol/L (1.5 wt.% based on crystallizer slurry) and the Al$^{3+}$ content was varied from 0 to 0.54 mol/L (1.1 wt.% based on crystallizer slurry). The runs were started by feeding pure reagents containing no impurity, the crystallizer containing the slurry of the previous run. The experiments consisted of four parts:

(a) No impurity was dosed for 2-2.5 hours (6 residence times)
(b) Impurity was dosed through the sulphuric acid feed for 2-2.5 hours
(c) No impurity was dosed for 2-2.5 hours
(d) Impurity was dosed through the sulphuric acid feed for 2-2.5 hours.

This experimental technique was used to ensure satisfactory reproducibility of results.

The viscosity and density of the phosphoric acid solution were found to increase as the concentration of Fe$^{3+}$ or Al$^{3+}$ increased. This effect was expected (Slack, 1968) for the following reason. In orthophosphoric acid, neighbouring PO$_4$ tetrahedra are held together by hydrogen bonds. Water tetrahedra which are considerably larger, cause distortion of the PO$_4$ lattice structure and reduce its rigidity. Therefore, the solution viscosity and density are reduced. Ions such as Fe$^{3+}$ and Al$^{3+}$ polarize the surrounding molecules which strengthens the hydrogen bonds and hence stabilizes the lattice structure. The viscosity was found to double.
by the addition of about 0.5 mol/L of the impurity. The presence of 0.5 mol/L impurity caused a density change of about 5%.

The change in the specific resistance of the gypsum cake with impurity concentration was the most significant result found in this study. Consistent systematic results due to the impurities were observed. The specific resistance was found to decrease with increasing impurity concentration at low impurity levels (0 to 0.15 mol/L) but increase with increasing impurity concentration at high impurity levels (> 0.25 mol/L). The minimum specific resistance was obtained in the range 0.15-0.25 mol/L impurity concentration. As the viscosity of the solution increased with the impurity concentration, the filtration rate was reduced at a constant specific cake resistance. The net effect of the impurity concentration on the filtration rate, and hence on the filtration time was represented by the product of the specific cake resistance and viscosity. The filtration time was initially reduced, reaching almost one-half that of the pure solution at impurity levels around 0.15-0.25 mol/L, while at the highest impurity levels, the filtration time was more than 3 times longer.

The chemical composition of the crystals was measured to examine the presence of impurities in the crystals. The concentration of the impurity in the gypsum was found to increase as the concentration of the impurity in the solution increased, although the amount absorbed in the crystal was small enough to leave the concentration in solution almost unchanged. The amount of coprecipitated phosphate was also found to increase as the impurity concentration in the solution increased.

Scanning electron microscope photographs of the gypsum crystals obtained in the presence of differing amounts of impurities gave evidence that Fe$^{3+}$ and Al$^{3+}$ impurities had a clear effect on the size, shape and thickness of the crystals. These morphological observations were in general agreement with those reported by Sarig et al. (1981) and Budz et al. (1986), who examined the effect of Al$^{3+}$ on gypsum morphology in an aqueous solution not containing phosphoric acid.

The initial decrease in the specific resistance of the filter cake $\alpha$, was accompanied by a systematic increase in the average particle size, while the subsequent increase in $\alpha$ at high impurity levels was accompanied by a reduction in the particle size. This result gave further
evidence for the existence of an optimal impurity level, giving a minimum filtration resistance.

Overall, the effects of the impurities on the filterability of gypsum were found to be significantly different in the low and high impurity ranges. In the low impurity range, both $\text{Al}^{3+}$ and $\text{Fe}^{3+}$ acted to improve the filterability of the gypsum while in the high concentration range, the filterability was reduced. The $\text{P}_2\text{O}_5$ losses in the crystal also increased systematically with the impurity concentration.

Gilbert, (1966) explored the effects of some impurities on the habits of gypsum crystallized from phosphoric-sulphuric acid solutions. The materials used were typical strong acids from American Cyanamid’s Dorr-Oliver type phosphoric acid plant at Bradley, made from uncalcined Florida rock. Concentrations were adjusted with reagent grade materials: $\text{H}_3\text{PO}_4$, $\text{H}_2\text{PO}_4$, $\text{Al}_2\text{O}_3$, $\text{Fe}_2\text{O}_3$, $\text{H}_2\text{SiF}_6$, HF. The use of only reagent grade materials permitted improved control of the kind and amount of impurities.

The first phase precipitated in reagent grade systems was always calcium sulphate hemihydrate which transformed to gypsum after holding. The presence of hemihydrate limited the extent of supersaturation which could be attained for gypsum growth, and the habit of gypsum which recrystallized from these solutions was the same, regardless of the $\text{P}_2\text{O}_5$ and $\text{H}_2\text{SO}_4$ concentrations. Gypsum was only crystallized from these solutions when gypsum seed was present. When plant acids were used, the initial phase precipitated was always gypsum in the range of the $\text{P}_2\text{O}_5$ and $\text{H}_2\text{SO}_4$ concentrations studied.

Although calcium sulphate hemihydrate was the first material to precipitate from reagent grade solutions of phosphoric-sulphuric acids, it was possible to force the precipitation of gypsum by the addition of impurities to the acid solutions. Various combinations of impurities were added to a solution containing 28% $\text{P}_2\text{O}_5$ and 1% $\text{H}_2\text{SO}_4$, which resulted in the precipitation of different phases, (i.e. hemihydrate, gypsum or both hemihydrate and gypsum).

A factorial experiment was run to investigate the effects of foreign ions in plant acid on the gypsum habit. Three levels of $\text{P}_2\text{O}_5$ concentration (27.7, 29.8 and 32.2%) and two levels each
of Al₂O₃, Fe₂O₃ and H₂SiF₆ were used. The major conclusion drawn was that in samples containing the higher level of aluminium, the habit of the gypsum crystals was drastically altered. The crystals in these samples were much smaller and less elongated. The other impurities in wet process phosphoric acid such as iron, silicofluoride and organic material were all found to have major effects on the crystallization of calcium sulphate and also affect the relative stability of gypsum and hemihydrate.

In this production process, control of the crystallization depends on the control of supersaturation because there is little control over the impurities entering the system except by changing the source of the phosphate rock. However, knowing the effects of the impurities enables anticipation of the changes caused by change of the rock source. The crystallization can then be optimized by making changes in operation to adjust the supersaturation.

Amin and Larson, (1968) performed experiments using a continuous mixed suspension, mixed product removal crystallizer to investigate the effects of temperature, phosphoric acid concentration, suspension density, supersaturation and residence time on the kinetic rates of growth and nucleation.

A number of experimental runs were made at different temperatures (45-80°C) and at a phosphoric acid P₂O₅ concentration of 42%. Experiments were carried out with a reagent grade system and a commercial grade system. The growth rate was found to increase with increasing temperatures while the nucleation rate decreased. Hemihydrate had a higher relative growth rate and a lower relative nucleation rate than gypsum. Therefore, larger crystals were obtained when calcium sulphate was crystallized in the hemihydrate form.

The effect of phosphoric acid concentration on the growth and nucleation was non-measurable as long as the concentration was held within the region in which a single compound was formed, i.e. hemihydrate or gypsum.

Experiments were conducted at 70°C and 42% P₂O₅ concentration, at different residence times, under conditions which gave a slight excess of calcium ions. Hemihydrate was the main crystal produced. Due to the growth and nucleation kinetics of gypsum however,
longer residence time and more precise condition control would be necessary to obtain the desired crystal form. Different residence times resulted in the generation of different supersaturation and consequently different growth and nucleation rates. A comparison of two runs made at 12 and 45 minute holding times respectively, showed a larger sized product for the long holding time and consequent low supersaturation. The size enhancement was primarily due to the fact that the nucleation rate decreased to a greater relative degree than the growth rate, when the holding time was increased from 12 to 45 minutes.

Experiments run at two suspension densities, 1.525 and 3.76 at 70°C and 42% P₂O₅ to produce hemihydrate, showed that an increase in particle size resulted from an increase in the suspension density.

The results from this study showed that the crystallization of calcium sulphate as hemihydrate had several advantages. The most important advantage was the fact that the hemihydrate had a much higher growth rate and a much lower relative nucleation rate than gypsum. The combined effect of these properties was that a larger average crystal size could be obtained in a shorter holding time. In addition, a more concentrated acid was produced which reduced the concentration required to produce product acid. A more suitable habit was formed and was less prone to modification by impurities or concentration effects. The hemihydrate formed was easily filtered and washed free of the phosphate. Hydration of the hemihydrate in the filter was not found to be a problem, however, in a commercial application, this may be troublesome.

2.3.4 Gypsum Crystallization - Citric Acid Process

A study by Sohnel et al. (1991) on gypsum crystals formed from the decomposition of calcium citrate, forms a contribution to the collection of literature sourced with regard to gypsum crystals produced during citric acid production. The decomposition of an aqueous suspension of calcium citrate by sulphuric acid, according to the following chemical reaction was studied:

\[
\text{Ca}_3\{\text{C}_6\text{H}_5\text{O}_7\}_2 \cdot 4\text{H}_2\text{O} + 3\text{H}_2\text{SO}_4 + 2\text{H}_2\text{O} \rightarrow 3\text{CaSO}_4 \cdot 2\text{H}_2\text{O} + 2\text{C}_6\text{H}_8\text{O}_7
\]  

...............(2.2)
This reaction represents an important technological step in citric acid production, as the resulting solid gypsum (CaSO₄·2H₂O) suspended in an aqueous solution of citric acid is then filtered off and citric acid is crystallized from the filtrate. Therefore, the decomposition of calcium citrate should be carried out under conditions ensuring the minimum filtration resistance of gypsum, i.e. conditions ensuring formation of the largest possible gypsum crystals.

The study aimed at determining the effect of both the decomposition temperature and the duration of solid phase contact with the liquid phase, on the physical properties of the formed gypsum particles and at explaining the process controlling mechanism.

200 g of an aqueous suspension containing 25 wt.% calcium citrate tetrahydrate was placed in a flask equipped with a reflux condenser and a stirrer. The flask was placed in a constant temperature water-bath at 25, 40, 60, 80 or 100°C respectively. 72.3 g of 50 wt.% H₂SO₄ was rapidly added to this suspension and the resulting mixture vigorously stirred for 7 hours with suspension samples withdrawn at intervals.

The particle size distribution of the formed gypsum crystals was found to shift towards larger sizes with increasing decomposition temperature. The same trend, i.e. the higher the temperature, the larger the crystals formed, was detected at all times during the 7 hour suspension stirring period.

The concentration of dissolved calcium in the mother liquor after calcium citrate decomposition, i.e. in an aqueous solution of citric acid, reached a constant value within approximately 2 hours of the start of the reaction although the concentration changes after 1 hour were rather insignificant. However, when decomposition at 100°C took place, a constant calcium concentration in the mother liquor was reached after approximately 5 hours.

The concentration of calcium in the mother liquor, i.e. 17 wt.% aqueous solution of citric acid monohydrate, determined after 7 hours of reaction duration was 0.6, 1.0, 1.0, 1.4 and 1.8 g/l at 25, 40, 60, 80 and 100°C respectively.

Observation of the gypsum crystals under an optical microscope showed that the crystal shape gradually changed from thin needles to well-developed elongated flat crystals during
solid contact with the mother liquor. The crystal size increased for approximately 4 hours of solid contact with the liquid.

The median of the gypsum particle size distribution shifted significantly towards larger sizes for about 4 hours of their contact with the mother liquor at constant temperature. However, the concentration of calcium dissolved in the mother liquor decreased substantially for just about 1 hour of reaction duration. Therefore, crystal growth due to deposition of excess solute from the mother liquor, represented a mechanism responsible only for the initial crystal size increase. Since the decomposition was practically complete within 1 hour of reaction commencement and the mother liquor then contained almost no excess of dissolved gypsum over equilibrium, the same mechanism could not be responsible for a further increase of the particle size distribution.

Agglomerate formation was not revealed from observation of the suspension under an optical microscope, only larger individual crystals were detected with progressing time. In addition, the total specific surface area of the solid (determined by nitrogen adsorption), decreased with an increase in crystal size, whereas agglomeration would result in an increase in particle size while the total surface area of the agglomerated solid remained constant (Gregory, 1984). As no further deposition of solute from the mother liquor took place, the described behaviour of gypsum crystals during their contact with the mother liquor was caused by the growth of larger crystals at the expense of smaller crystals. This process is referred to as ripening. In support to this conclusion was the observed increase of volume fraction of large particles with time, while the fraction of small particles remained unchanged. The changes of particle size distribution with time was caused by the continuous dissolution of smaller crystals and deposition of this material on large crystals (Gutoff et al., 1974).

In conclusion, Sohnel et al. (1991) found that in order to prepare a gypsum suspension with the optimum filterability, the decomposition of calcium citrate should be carried out at a high temperature and the resulting solid should be in contact with the mother liquor for about 4 hours.
Literature by Savchenko et al. (1973 and 1974) described studies on gypsum crystals produced during citric acid production. One study determined the factors which minimise the solubility of calcium sulphate in citric acid solutions, (1973).

An excess of calcium sulphate dihydrate crystals were placed at the bottom of a vessel and citric acid solutions (3-30%) were added and mixed (60 rpm) at temperatures of 40, 50, 60, 70, 80 and 90°C. It was found that the solubility of calcium sulphate dihydrate increased with increasing temperature. The highest solubility increase (20-25%) was observed where the citric acid concentrations were 10-30%.

The solubility of calcium sulphate dihydrate was also determined in 20% citric acid solutions containing 0.1-20% free sulphuric acid at temperatures of 40, 50, 60, 70 and 80°C. This was used to characterize the four component system \( \text{CaSO}_4 \cdot \text{H}_2\text{SO}_4 \cdot \text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O} \). The solubility of \( \text{CaSO}_4 \cdot 2\text{H}_2\text{O} \) was found to decrease sharply at low concentrations of sulphuric acid, the minimum solubility reached with a concentration of 1%. Then with increasing the concentration of \( \text{H}_2\text{SO}_4 \) above 1%, the solubility was increased (maximum with 10% concentration). As the temperature increased, the solubility of \( \text{CaSO}_4 \cdot 2\text{H}_2\text{O} \) was found to increase.

The influence of temperature and free sulphuric acid on the solubility of gypsum applicable to pure citric acid solutions was also found to apply to production solutions. Therefore, to decrease the concentration of calcium ions in production solutions of citric acid, the temperature was reduced. In addition, the process of calcium citrate decomposition was carried out with the citric acid solution containing a small amount (0.1-0.5%) free sulphuric acid.

A surplus of sulphate ions in citric acid solution resulted in the creation of large crystal gypsum sediment. However, it was necessary to control the composition of created solutions thoroughly because a significant surplus of sulphuric acid would cause an increase in the corrosive activity of the solution.

A second study by Savchenko et al. (1974) researched the process of hydration of calcium sulphate hemihydrate (\( \text{CaSO}_4 \cdot 0.5\text{H}_2\text{O} \)) in citric acid solutions at temperatures of 50, 70 and
90°C. CaSO₄·0.5H₂O crystals containing 6.187% water of crystallization were placed in citric acid solutions (10, 25 and 30%) at the various temperatures and agitated at 30 rpm. Hydration in the presence of CaSO₄·2H₂O priming crystals in a 25% citric acid solution was also investigated. The CaSO₄·0.5H₂O crystals reached full hydration after 30 minutes. An increase of the system temperature from 50 to 90°C resulted in acceleration of the process. The presence of calcium sulphate dihydrate priming crystals significantly reduced the speed of hydration of CaSO₄·0.5H₂O. Therefore, together with an increase in temperature, the addition of priming crystals can be used in production conditions for acceleration of the calcium sulphate hemihydrate hydration process.

The process of hydration of calcium sulphate hemihydrate was accompanied by dissolution of initial crystals (period I) and formation of calcium sulphate dihydrate (CaSO₄·2H₂O) crystal structure and the growth of gypsum crystals (period II). The kinetics of calcium sulphate crystals growing in the process of calcium citrate decomposition by sulphuric acid at different temperatures and citric acid solution concentrations were studied. The process of gypsum crystals ripening amounted to no more than 60 minutes. Therefore, period II, connected with the growth of created calcium sulphate hemihydrate crystals, took about 30 minutes.

Cleaning of production solutions from trivalent ferrum ions was achieved by deposition in the form of Berlin Blue Fe₄[Fe(CN₆)]₃ with the help of calcium ferrocyanide. Ferrocyanide was added to the solution immediately after completion of the calcium citrate decomposition by sulphuric acid. Therefore, the origin of Berlin Blue coincided with the initial stages of gypsum sediment formation (period I). In this case, co-crystallization of gypsum and Berlin Blue was inevitable and was followed by an impediment of gypsum crystal growth due to high-charge ions [Fe(CN₆)]⁴⁻ adsorption on particle surfaces and an increase in the number of crystallization centres. This resulted in the formation of a high dispersive sediment with poor filtration quality.

Research into Berlin Blue deposition during different periods of gypsum crystallization was carried out. The concentrations of citric acid solutions formed during calcium citrate
decomposition varied within the range 215-220 g/l in all tests. A certain dependence existed between the period of ferrum ions deposition, crystal radius and the resulting filtration rate. The rate of suspension filtration was found to be most important during the deposition of ferrum ions at the end of period II, being influenced not only by the dispersion of gypsum crystals, but also by the nature of the Berlin Blue sediment.

To improve the filtration properties of gypsum suspensions, it was found to be advantageous to carry out ferrum ions deposition from citric acid solutions, not immediately following full citrate decomposition, but 50-60 minutes after the addition of acid to the citrate suspension (i.e., after completion of the gypsum sediment ripening process).

Schulz, 1974 invented an improved process of isolating citric acid from strongly contaminated citric acid solutions by means of electro-dialysis. The invention also related to an improved process of isolating and purifying alkali metal citrates of remarkable purity from fermentation solutions. This involved isolating citric acid from the fermentation solution in the form of its alkali metal salt and recovering the acid from such salts in a single operation. An advantageous feature of the invention was that considerable savings in chemicals were achieved and the amount of waste gypsum was considerably reduced. Ready filterable gypsum crystals were formed due to the presence of alkali metal ions. The gypsum produced by reacting mono-alkali metal calcium citrate with sulphuric acid was found to filter about five or six times more rapidly and was also more rapidly washed than gypsum produced in the absence of alkali metal ions. The amount of water required to completely wash the gypsum was also reduced by about 20-25%.

The citric acid fermentation solution was concentrated by evaporation and neutralized to a concentration of at least 40% calculated for free citric acid. In general, the citric acid fermentation solution was neutralized by the addition of the respective alkali metal hydroxide bicarbonate or carbonate in an amount sufficient to produce a salt of the composition of the desired crystals. The alkali metal salts crystallized on standing or on slowly stirring the solution (seed crystals were preferably added). Crystallization was completed within 48 hours and separation of the crystals was achieved by centrifuging. Washing the crystals with
a small amount of water resulted in an almost white or yellowish-brown crystalline precipitate, depending on the type of alkali metal citrate recovered.

The yield of citric acid when recovered in the form of its alkali metal was between about 50 and 80%, depending on the selected salt. Citric acid which remained in the mother liquor together with most of the impurities, was recovered by precipitation in the form of a calcium salt, (preferably in the form of mono-alkali metal calcium citrate.) The precipitated mono-alkali metal calcium citrate was more readily filterable than tri-calcium citrate and calcium mono-hydrogen citrate, which were previously precipitated as intermediate products. The resulting mono-alkali metal calcium citrate was then reacted with 1 mole of sulphuric acid calculated for 1 mole of citrate to produce a mono-alkali metal citrate solution and gypsum.

When recovering citric acid by means of tri-calcium citrate, 1.5 moles of sulphuric acid were required per mole of citric acid, recovery in the form of calcium mono-hydrogen citrate required 1 mole of sulphuric acid for 1 mole of citric acid, while this invention consumed only 0.5-0.2 moles of sulphuric acid per mole of citric acid, depending on the yield of the alkali metal citrate.

The solution obtained after filtering the gypsum contained in general, only the mono-alkali metal di-hydrogen citrate. The solution was then further worked up to citric acid, either as such, or preferably together with the alkali metal citrate crystals. If the crystalline product initially obtained from the concentrated citric acid fermentation solution was also the mono-alkali metal di-hydrogen citrate, it was dissolved in the filtrate obtained from the gypsum filtration. The resulting solution of mono-alkali metal di-hydrogen citrate was then further worked up to citric acid.

The working up was achieved by either percolation through a number of columns containing cation exchange material in the hydrogen form, or alternatively, the citric acid was recovered by electrodialysis. Electrodialysis had the further advantage of permitting recovery of the alkali metal compound used for neutralizing the citric acid fermentation solution.

The reactions involved in the invention were illustrated by the following reaction equation sequence:
Ishikawa et al., 1972, invented a method of production of neutral gypsum by reaction of either dilute sulphuric acid or a solution containing sulphuric acid with lime or slaked lime, where the addition of citric acid facilitated the formation of easily dehydratable coarse columns or thick plates of gypsum crystals. Under normal circumstances, gypsum in the shape of needles, columns or plates were observed.

Prior to the invention, when gypsum was obtained by reacting lime or slaked lime with a sulphuric acid solution, thermodynamic temperatures of 100°C or higher, 95°C or higher, 85°C or higher and 65°C or higher for sulphuric strengths of 100, 200, 300 and 400g/l respectively were required for the reaction to produce hemihydrate gypsum. After that, plate-like gypsum as crystal seed was added and the temperature lowered to that at which dihydrate gypsum re-crystallized. At this recrystallization time, the crystal seeds facilitated the production of plate-like gypsum. With a sulphuric acid concentration less than 100g/l however, even with a thermodynamic temperature in excess of 100°C, the hemihydrate gypsum was not easily formed and most of the crystals were small and needle-shaped.

To overcome the disadvantages of small, needle-like crystals, the sulphuric concentration was increased above 100g/l, temperatures of 70-100°C were used and plate-like seed crystals were
introduced to aid re-crystallization. Large crystals were produced by this method but it involved a two-stage process which made it very inefficient.

The invention removed the limitations from the production process so that even when the sulphuric acid concentrations and the thermodynamic temperatures were both low, large gypsum crystals were produced directly in a single process without the addition of seed crystals.

The main feature of the invention was the addition of the proper quantity of citric acid to a sulphuric acid solution or a solution containing sulphuric acid. This enabled a neutral reaction between the sulphuric acid and lime or slaked lime. By measuring both the speed of nucleic formation and the speed of nucleic propagation, and by observing the changes in crystal shattering characteristics, coarse columnar and plate-like neutral gypsum crystals with good dehydration characteristics were produced directly in one process.

The discovery proved that concentrations of dilute sulphuric acid below 100g/l could be used to produce large gypsum crystals. For valid results, the quantity of citric acid added was in the range of 0.1-2.0% of the volume of sulphuric acid solution. When less than 0.1% of citric acid was added, virtually no effect was observed and if greater than 2% was added, the effect was no more pronounced. The appropriate temperature range for gypsum production was between 20 and 70°C. Above 70°C, the production became economically unviable and was unnecessary. Below 20°C, the formation of large crystals was slowed down and was therefore inappropriate.

A practical example clearly illustrated the benefits of the discovery. 100g of citric acid was added to 10 litres of citric acid solution with a concentration of 30g/l and heated to 50°C. 150g of powdered lime was gradually added while stirring and after the reaction, the stirring was stopped and left to mature for three hours. On cooling, the size of the gypsum crystals produced were measured. The length increased from a size range of 10-30μm without citric acid, to a range of 100-150μm with the citric acid. The width increased from 1-3μm without the citric acid, to 75-100μm with the citric acid, while the thickness increased from 1-3μm without the citric acid, to 20-30μm with the citric acid.
2.3.5 Gypsum Crystallization - General

A study by Van Rosmalen et al., 1981 aimed at finding a convenient description of the growth process of gypsum, by comparing three selected methods of analysis (independent linear rate method, mean linear rate method and second order rate method), and finding evidence for the growth mechanism of gypsum. Only the independent linear rate method gave an adequate description of the growth process. The method was based on the relationship between the overall growth rate, the linear growth rates of the different crystal faces and the normalized volume of the crystals. The linear growth rate of a crystal face is usually defined as the linear rate of normal displacement of that face relative to a fixed point in the crystal. For large crystals, it was evident that the linear growth rate did not depend on the geometry of the crystals but for small crystals, it was not. The dependence however was unknown.

The growth mechanism of gypsum was explained by a combined spiral growth and layer mechanism. Gypsum apparently formed layers, originating from screw dislocations. In the case of gypsum, many small crystals of different shapes and sizes are formed under various conditions. Foreign ions and molecules can have a large influence on the morphology, habit, twinning and therefore on the growth rate of the crystals.

Supersaturation and impurities are well known to influence the morphology and degree of perfection of gypsum crystals (Edinger. 1973). When gel growth was compared with growth from solution, one of the main differences was caused by the degree of supersaturation. When single crystals of slightly soluble salts were grown from highly supersaturated solutions which just remained stable over longer periods, by slow evaporation or cooling, the crystals never became large because the supply of dissolved compound to the crystal surfaces was still very small. Since larger crystals were grown in a gel, the supersaturation near the surface of the crystals must be higher in a gel than in a solution. It was explained by the highly nucleation suppressing character of a gel (Henisch, 1970). This suppression was due to the envelopment of the heterogeneous nuclei, leaving only homogeneous nucleation, which occurred at higher supersaturations.
Van Rosmalen and Marchee, 1976, grew single crystals of gypsum up to 0.25 cm\(^3\) with the gel method and characterized the crystals in relation to the growth conditions. The influence of impurities on the habit of gypsum were also reported.

Two inorganic silica gels and one organic agar gel were used. One silica gel was prepared from sodium metasilicate and hydrochloric acid, diluted to a SiO\(_2\) concentration of 0.25M. The other silica gel was obtained by treating a 0.5M sodium metasilicate solution with a strongly acid cation exchanger to a pH of about 4.5. The final SiO\(_2\) concentration after dilution was also 0.25M. The main advantage of this pure silica gel was that all additives to the gel could be chosen freely. The agar gel was prepared by dissolving 0.5 wt.% agar in water.

U-tubes with a diameter of 18mm were used in most experiments. The gel volumes were about 30-40 ml. The arms of the tubes were filled with solutions of 0.5-2.0 M CaCl\(_2\) and Na\(_2\)SO\(_4\) respectively. The tubes were placed for 5 to 7 months in water baths thermostated at 25°C. An adapted amount of solute was added to the pure silicic acid to prevent shrinking of the gel volume by osmosis.

Most crystals were grown in the ion-exchanged silica gel and needles were formed either separately or as a cluster. Needles grown as a cluster showed well-shaped terminating faces, while separately grown crystals were mostly terminated by rounded tops. Intermediate forms between large, well defined terminating faces and rounded tops were also noticed, showing small terminating faces which covered only the basis of the further rounded top.

Due to the higher "consumption" of supersaturation by the cluster of crystals than by a separate crystal, the supersaturation close to the crystal surface of the cluster was lower than the supersaturation close to the surfaces of separate crystals.

All crystal surfaces (even the terminating faces) were very smooth. The bulk of the crystals appeared to be optically perfect and no inclusions were noticed under a microscope. Autoradiograms which showed only ion-exchange with the surface layers of the crystals, proved the absence of lattice imperfections since at room temperature, only lattice defects caused a measurable solid state diffusion of ions into the bulk of the crystal.
With the gel method, the concentrations of the reagents and the concentration of NaCl in the gel varied through the tube and with time. The pH also changed for some additives, like HCl. This gave a variation in the solubility and supersaturation. However, needles were always obtained and the impurities studied always had the same influence on the habit.

When NaH$_2$PO$_4$, an unavoidable impurity present in gypsum obtained as a by-product of the fertilizer manufacture, was added to the gel, needles also developed but showed elongated inclusions along the C-axis. When an organic compound was added, a more stubby habit of the gypsum crystals was obtained. Shapeless untransparent lumps developed when keratine (used as a setting retarder in the transformation of hemihydrate into gypsum) was suspended in the gel. Stubby shaped crystals grew when sodium citrate (another setting retarder) was added to the CaCl$_2$ solution. Gypsum crystals grown in the presence of lactic acid were shaped like short broad rods and formed less clusters. In this case, not only an organic anion was added, but H$_3$O$^+$ ions were also added. The addition of tris (hydroxy-methyl) amino methane (THAM), often used as a buffer solution gave rods instead of needles.

Crystals grown in agar were equantly shaped (roughly equal sizes in the three dimensions). A lot of transparent crystals were found among the smaller ones (max. sizes of approx. 2 by 3mm) and only the more perfect crystals also developed terminating faces. The larger crystals with maximum sizes of about 5 by 10mm were all opaque. Twinning was never noticed. Some faces of the bright crystals were as smooth as those of the needles while the non-transparent crystals showed faces covered with macro steps and kinks. The non-transparency of the crystals was apparently caused by inclusion of the agar gel because the analysis of these crystals showed some carbon content. The X-ray transmission patterns from the bright crystals were found to be exactly the same as those taken from the needles, while the patterns taken from the opaque equants consisted of elongated spots in a radial direction (attributed to lattice bending).

An experiment in which small amounts of hydrochloric acid were added to both reagents above the agar gel, revealed that needles were grown instead of equants. The needles were shorter than those grown in silica gel.

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Overall, the gypsum crystals grown in silica gel were in general, more perfect than those grown in agar. Their surfaces were smoother, less inclusions were incorporated and less distortion of the crystal lattice occurred. Some organic compounds had the tendency to change the crystal habit from a more elongated needle-like shape into a more stubby appearance. Depending on the organic compound, the modification varied from a shortening of the needles to the development of tabular shaped crystals. However, H$_3$O$^+$ ions promoted the needle shape. Since only traces of organic compounds may influence the crystal habit, care must be taken in drawing conclusions about the components which finally determine the crystal habit.
Chapter Three

Plant and Process Familiarisation
3.1 Introduction

This chapter contains a description of the recovery process at ADM. (In order to respect ADM's confidentiality, the level of process detail provided in this thesis is limited). A thorough understanding of the process from an early stage in the project had a direct bearing on the overall project progress. Details of a comprehensive database are also included. The development of this database aimed at gaining an increased familiarity of the plant, creating a knowledge of the normal operating conditions and control parameters, forming a more thorough understanding of the existing gypsum production process and identifying the variation of crystal shape and size distribution along the formation path. During formation of the database, the crystal habits of both calcium citrate and gypsum were detected and the trends and variations in crystal size throughout the recovery process were identified. Trials with the vortex mixer off-line illustrated the increase in particle size attainable without the vortex mixer. An improvement in the gypsum filtration rate during these trials without the vortex mixer was also confirmed, as well as an increase in the quantity of hemihydrate gypsum present in the filtrate. Overall, the development of this database enhanced the technical understanding of the gypsum production process and provided an improved knowledge of the issues to be addressed throughout the project.

3.2 Process Description

3.2.1 Introduction

The citric acid production process is divided into three main stages: fermentation, recovery and refining. The process begins with the fermentation of molasses, the recovery process involves recovery of citric acid from the fermentation broth, and the resulting aqueous acidic solution is crystallized in the refining process to give the finished product citric acid. The main emphasis of this project is on the recovery of citric acid, in particular, the gypsum formation step.

Molasses is the raw material used for the production of citric acid. The citric acid broth entering the Recovery process from the Fermentation process contains citric acid in solution
and both soluble and insoluble impurities. Yeast and insolubles are removed to give clarified broth. The citric acid broth is blended with mother liquor which is recycled from the refining process. On dilution, the broth deposits high molecular weight colour bodies which are removed. The broth going forward through the recovery process is known as *centrate* or *suciac* and contains Hydrous Citric Acid and both inorganic and organic impurities all in solution. The soluble impurities are removed from solution using the “calcium citrate process” during which the majority of the citric acid in the feed liquor is converted and precipitated as calcium citrate. The calcium citrate crystal slurry is filtered and washed. The calcium citrate cake discharge is reslurried in the second stage filter repulper. A recycle stream from the strike tank (see Section 3.2.2) is used to reslurry the cake. The material is pumped from the repulper to the strike tank for continuous decomposition with sulphuric acid to produce gypsum.

### 3.2.2 Gypsum Formation

Calcium citrate is decomposed in the strike tank\(^1\) with concentrated sulphuric acid to give gypsum and a solution of citric acid. The reaction is known as the *sour reaction*. A portion of material from the strike tank is recycled to the repulper to slurry the calcium citrate cake. The remaining contents of the strike tank are pumped to the trim tank\(^2\). The flowrate from the strike tank is controlled to maintain a constant level in the strike tank. The final pH adjustment on material from the strike tank is carried out in the trim tank. The contents of the trim tank are then pumped to the gypsum filter feed tanks. Again, the flowrate from the trim tank is controlled to maintain a constant level in the trim tank.

The pH at which the strike tank is controlled and the sulphuric acid flowrate to the strike tank is critical. If the pH is too high, i.e. if the sulphuric acid flowrate is too low, a thick, heavy slurry results which trips out the strike tank agitator and the calcium citrate filter repulper. If the pH is too low, i.e. if too much sulphuric acid is added, small, needle type gypsum crystals are formed which cause poor gypsum filtration, thus reducing the filtration rate.

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1. Strike Tank - The main gypsum reaction tank where most of the sulphuric acid is added.
2. Trim Tank - The second gypsum reaction tank where the remaining sulphuric acid is added to trim the pH.
A slight excess of $\text{H}_2\text{SO}_4$ is used (approximately 1% over the stoichiometric amount required for decomposition of the calcium citrate). This excess is required to enhance crystallization in the refining end of the plant. Too much sulphuric acid has a detrimental effect on the crystallizer bank operation and also causes corrosion problems as dilute sulphuric acid is highly corrosive. Therefore, the final pH of the sour reaction is extremely critical.

At present, the calcium citrate slurry and $\text{H}_2\text{SO}_4$ are mixed in a vortex mixer prior to being introduced to the strike tank. Figure 3.1 illustrates the vortex mixer in place at ADM.

![Figure 3.1: Vortex Mixer at ADM Ringaskiddy](image)

The mixer is positioned over the strike tank and used to mix the calcium citrate slurry with sulphuric acid before entering the strike tank. A schematic view of a vortex mixer is given in Figure 3.2. The vortex mixer is a flat cylindrical chamber with the process streams introduced at tangents to the circumference and with the mix discharged at the centre, bottom.

The process advantages of fluidic vortex mixing for this reaction are short mixing time and the effective dispersion of small volumes into significantly larger volumes. A more consistent precipitate should be obtained because the mixing is completed before the nucleation of crystals takes place. The problems of product burning leading to colour
formation, and a wide range of supersaturation values leading to particle size variation, should be essentially eliminated.

![Schematic View of a Vortex Mixer](image)

Figure 3.2: Schematic View of a Vortex Mixer

The gypsum produced in the sour reaction step is insoluble and is removed from the citric acid liquor (known as the *sour liquor*) at the gypsum filtration step using a *pannevis* filter (see Appendix A) and disposed of. The filtrate obtained from this step is known as the *sour filtrate* and is composed mainly of citric acid in solution (contains approximately 35-40% w/w Hydrous Citric Acid). This filtrate is retained for further purification and crystallization in the refining process.

The gypsum filtration system is a major step in the citric acid recovery process, therefore the throughput must be maintained at a rate which will keep the downstream steps in the plant running at optimum conditions. Since the gypsum filtration system is also one of the loss areas in the plant, the system must be balanced so that production is at a maximum and that the citric acid loss in the disposed gypsum is at the minimum acceptable level (<0.7%).

The filtrate from the pannevis filter is essentially citric acid with a composition of approximately 35%-40% HCA. The citric acid mother liquor is evaporated and then filtered in *pressure leaf* filters (see Appendix A) in order to remove any solids present at this stage (approx. 1.5-2%). The mother liquor then goes through a series of crystallization, filtration and treatment steps before reaching the finished goods crystallizer where the final product is crystallized out as Hydrous or Anhydrous Citric Acid.
3.3 Development of Plant Database

3.3.1 Introduction

This section describes the development of a detailed plant database on the gypsum production step. The objectives of this work were to:

- gain familiarity with the operating conditions and control parameters.
- form a thorough understanding of the existing gypsum production process.
- identify the influence of process parameters on the crystal characteristics.
- identify the variation of crystal shape and size distribution along the formation path.

The database was developed in two stages:

Stage 1 involved monitoring the plant operating conditions at a series of time intervals over a 12 day period. In addition, on each day, samples of gypsum slurry were taken from the gypsum filter feed tank for particle size measurement.

Stage 2 was carried out on selected days over a total period of two months. Each day, the plant operating conditions were checked to ensure relatively stable operating conditions and important plant operating parameters were noted at this stage. Samples were then taken along the gypsum formation path and a series of laboratory tests and analysis performed. Details of the laboratory analysis can be found in Chapter 4. Prior to stage 2, the laboratory work was performed on a trial basis for a period of a week to ensure competency in the sampling and analysis techniques. This ensured accurate laboratory data for inclusion in the database.

3.3.2 Stage 1

The main objective of this stage was to investigate the change in plant conditions on a daily basis as well as to identify the changes occurring from day-to-day. A series of recordings were made at a number of times each day and various graphs plotted from the data to investigate any significant trends. The particle size of the gypsum slurry was also measured and recorded each day. The following parameters were recorded from the control room during stage 1:
Chapter Three - Plant and Process Familiarisation

- Strike and Trim Tank Temperatures
- Strike Tank pH
- Trim Tank Conductivity
- Sulphuric Acid Flowrate to Strike and Trim Tanks
- Ratio of Sulphuric Acid Flow (Strike : Trim Tank)
- Recycle Flowrate from Strike Tank to Calcium Citrate Filter Repulper
- Gypsum Filtration Rate
- Specific Gravity of Filtrate from Gypsum Filtration Step

The actual data recorded is shown in Table 3.1 and the corresponding graphical analysis is illustrated in Figure 3.3.

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<th>H₂SO₄ to Trim (GPM)</th>
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Table 3.1: Recordings from Database Development - Stage 1
Chapter Three - Plant and Process Familiarisation

Variation in Strike & Trim Tank Temperature

Variation in Strike Tank pH & Trim Tank Conductivity

Variation in Sulphuric Acid Flowrates

Variation in Sulphuric Acid Ratio

Variation in Recycle Flowrate

Variation in Specific Gravity

Variation in Gypsum Filtration Rate

Variation in Mean Particle Size

Figure 3.3: Graphical Representation of Plant Recordings - Stage 1
From Figure 3.3, it is obvious that a considerable fluctuation in operating conditions was observed during production, even over a single day. The influence of production conditions in other areas of the plant were also seen to have an influence on the gypsum production step. Therefore, due to the amount of influencing factors present in the production area, a continuous variation in process parameters was experienced and so, quantification of any trends or observations was difficult.

The particle size of gypsum was measured each day and the distribution of particles examined. The mean particle sizes obtained, as well as the 10% and 90% cut-off points are given in Table 3.2.

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Table 3.2: Malvern Particle Size Data - Stage 1
The data in Table 3.2 is represented graphically in Figure 3.4. Although the particle size distribution varied from sample to sample, the overall trend appeared to maintain relatively constant within limits during the data collection period.

![Graphical Representation of Malvern Particle Size Data - Stage 1](image)

**Figure 3.4: Graphical Representation of Malvern Particle Size Data - Stage 1**

The following observations were made from the data collected:

- From the analysis carried out in stage 1 alone, it was not possible to draw any definite conclusions about the influence of various plant operating parameters on the actual gypsum particles, due to the fluctuations in process parameters during the plant monitoring period.

- Further analysis of the gypsum formation stages was necessary to investigate any variations in the particles at different stages of the process.

Overall, stage 1 allowed a more detailed technical understanding of the gypsum production process to be obtained. The areas for further investigation were identified and addressed in stage 2.
3.3.3 Stage 2

This stage was carried out as a follow-up to stage 1. Since no significant trends or observations could be determined as a result of stage 1 alone, a more detailed plant study was performed. Recording of the plant operating conditions as for stage 1 was continued. In addition, the level percentages of the strike, trim and gypsum filter feed tanks were recorded in order to determine the residence time within these tanks. A series of plant samples were also taken as opposed to the single gypsum slurry sample taken during stage 1. The temperature and pH of the slurry samples was taken at the sampling time. The laboratory analysis performed on the samples, along with the documented plant parameters, established an improved understanding of the gypsum production process. The variation of crystal shape and size distribution along the formation path was also identified.

3.3.3.1 Plant Samples

The specific samples taken from the plant are explained below and are numbered from 1 to 10 in Figure 3.5. The same numbering system is used for illustration in the graphical analysis:

- Sample no. 1: Final calcium citrate reaction vessel
- Sample no. 2: Calcium citrate cake from 1st stage calcium citrate filter
- Sample no. 3: Calcium citrate cake from 2nd stage calcium citrate filter
- Sample no. 4: Calcium citrate cake slurried in recycle from strike tank
- Sample no. 5: Pipe-line to vortex mixer
- Sample no. 6: Gypsum slurry as it leaves the vortex mixer
- Sample no. 7: Gypsum slurry from the strike tank
- Sample no. 8: Gypsum slurry from the trim tank
- Sample no. 9: Gypsum slurry from pipe entering the 1st gypsum filter feed tank
- Sample no. 10: Gypsum slurry from pipe entering the 2nd gypsum filter feed tank
- Sample no. 11: Gypsum cake from the pannevis filter (or stand-by gypsum filters)
3.3.3.2 Laboratory Analysis

The following laboratory tests and analytical procedures were carried out, a detailed description of which can be found in chapter 4:

- Analytical Procedure no. 1: Malvern particle size analysis
- Analytical Procedure no. 2: Microscopic analysis and photograph record
- Analytical Procedure no. 3: Solids test
- Analytical Procedure no. 4: Filterability test
- Analytical Procedure no. 5: Measurement of potassium content in filtrate
- Analytical Procedure no. 6: Calcium citrate assay

3.2.3.3 Procedure Variations

During the database development, slight variations in procedure were introduced from day to day. These variations involved either the inclusion of an extra sample, or the elimination of a particular sample or analysis application for a specific reason. Therefore, for clarification purposes, the specific samples and analytical procedures applicable to each day are listed below:

- **Day 1:**
  - Plant Samples: 1, 3, 4, 6, 7, 8, 9, 10, 11.
  - Analytical Procedures: 1, 2, 3, 4, 5.

- **Day 2:**
  - As for day 1.

On days 1 and 2, a significant difference in the mean particle size was noticed between the calcium citrate sampled from the last calcium citrate reaction vessel and that filtered on the 2nd stage rotary filter. To investigate this further, a sample from the 1st stage rotary filter was also included in the analysis of the days following.

- **Day 3:**
  - Plant Samples: 1, 2, 3, 4, 6, 7, 8, 9, 10, 11.
  - Analytical Procedures: 1, 2, 3, 4, 5.

On day 4, the wet-end was shut down in the morning so sampling was not possible until the afternoon. Only selected samples were then taken for particle analysis.

- **Day 4:**
  - Plant Samples: 1, 2, 3, 4, 7.
  - Analytical Procedures: 1, 2.
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- **Day 5:** As for day 3.

After day 5, the trend obtained from the solids data was satisfactory for conclusion on the variation of solids percentage over the sample points. This test was therefore eliminated for days 6 to 9. For verification, the solids test was carried out again from day 10 onwards. Also, data collected from days 1 to 5 suggested that no significant changes were experienced between the sample taken from the vortex mixer exit and the samples taken from the series of tanks following it. Therefore, the samples from the strike tank and the 2nd gypsum filter feed tank (sample nos. 7 and 10 respectively) were eliminated from the continuing analysis.

Sample no. 2 was also eliminated for days 6 to 8.

- **Day 6:** Plant Samples: 1, 3, 4, 6, 8, 9, 11. Analytical Procedures: 1, 2, 4, 5.
- **Day 7:** As for day 6.
- **Day 8:** As for day 6.
- **Day 9:** Plant Samples: 1, 2, 3, 4, 6, 8, 9, 11. Analytical Procedures: 1, 2, 4, 5.
- **Day 10:** As for day 9.

On day 11, a trial was carried out with the vortex mixer off-line. Therefore, a sample from the strike tank replaced the usual vortex sample. The solids test was again included in the analysis. An additional sample point was installed in the pipe line from the calcium citrate filter repulper to the vortex mixer. A sample from this point (sample no. 5) was included in the analysis from day 11 onwards.

- **Day 11:** Plant Samples: 1, 2, 3, 4, 5, 7, 8, 9, 11. Analytical Procedures: 1, 2, 3, 4, 5.

The plant was operating with no vortex mixer from Jan. 6th to Jan. 24th due to the installation of a new vortex mixer in place of the existing mixer. While the installation was taking place, the opportunity was used to investigate further, the gypsum reaction without the vortex mixer. Sample analysis was carried out for 5 days without the vortex mixer in order to verify the results obtained from the trial on day 11 (without vortex). A variety of samples were taken over the 5 days and in addition to the previous analysis methods, the sour filtrate
going forward to the refining end was also examined. Only selected samples were taken on
day 12 and a calcium citrate assay (analytical procedure no. 6) was carried out on sample no. 4. Analysis of the potassium content in the filtrate (analytical procedure no. 5) was eliminated from the procedure at this stage.

- **Day 12:**
  - Plant Samples: 3, 4, 5, 9, 11.
  - Analytical Procedures: 1, 2, 4, 6.

- **Day 13:**
  - Plant Samples: 3, 4, 5, 7, 8, 9, 11.
  - Analytical Procedures: 1, 2, 3, 4.

On days 14 and 15, emphasis was placed on the sour filtrate. Samples of the filtrate were taken from the plant along with a single gypsum slurry sample (sample no. 9).

- **Day 14:**
  - Plant Samples: 9.
  - Analytical Procedures: 1, 3, 4.

- **Day 15:**
  - As for day 14.

A series of samples were again taken on day 16 and calcium citrate assays performed along the gypsum formation path. The sour filtrate was also analysed.

- **Day 16:**
  - Plant Samples: 4, 5, 7, 8, 9, 11.
  - Analytical Procedures: 1, 3, 4, 6.

The database development continued for an additional 4 days when the new vortex mixer was installed. The main analysis applied here was the measurement of particle size.

- **Day 17:**
  - Plant Samples: 5, 6, 9.
  - Analytical Procedures: 1.

- **Day 18:**
  - Plant Samples: 4, 5, 6, 7, 8, 10, 11.
  - Analytical Procedures: 1, 2, 4.

- **Day 19:**
  - As for day 18.

The analysis performed on day 20 was used to carry out a mass balance around the gypsum production step (see Section 3.4). Therefore, the densities of the samples were measured in addition to the normal analysis.

- **Day 20:**
  - Plant Samples: 1, 5, 6, 7, 8.
  - Analytical Procedures: 1, 3, 4, 5, 6.
3.3.3.4 Results

The actual data recorded during stage 2 is shown in Table 3.3 and corresponding graphical analysis is given in Figure 3.6.

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<thead>
<tr>
<th>DATE</th>
<th>Days</th>
<th>Strike Tank Temp. (°C)</th>
<th>Strike Tank Cond.</th>
<th>Trim Tank Temp. (°C)</th>
<th>Trim Tank pH</th>
<th>H_2SO_4 to Strike (GPM)</th>
<th>H_2SO_4 to Trim (GPM)</th>
<th>Recycle Rate (GPM)</th>
<th>H_2SO_4 Ratio</th>
<th>S.G.</th>
<th>Filtration Rate (GPM)</th>
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</thead>
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</table>

Table 3.3: Recordings from Database Development - Stage 2

From Figure 3.6, it is evident that fluctuations in operating conditions were also experienced during stage 2.
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Variation in Strike & Trim Tank Temperature

Variation in Strike Tank pH & Trim Tank Conductivity

Variation in Sulphuric Acid Flowrates

Variation in Sulphuric Acid Ratio

Variation in Recycle Flowrate

Variation in Specific Gravity

Variation in Gypsum Filtration Rate

Variation in Mean Particle Size

Figure 3.6: Graphical Representation of Plant Recordings - Stage 2
The mean particle size of the gypsum slurry from the 1st filter feed tank along with the 10% and 90% cut-off points are summarised in Table 3.4 as done previously for stage 1 (Table 3.2).

<table>
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<tr>
<th>DATE</th>
<th>Record No.</th>
<th>D(v, 0.5) (microns)</th>
<th>D(v, 0.1) (microns)</th>
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</table>

Table 3.4: Malvern Particle Size Data of 1st Gypsum Filter Feed Tank Sample - Stage 2

The corresponding graphical representation is shown in Figure 3.7.

Figure 3.7: Graphical Representation of Malvern Particle Size Data - Stage 2

It is interesting to note that the 10% cut-off point remained very constant during Stage 2. However, for the trials without the vortex mixer, both the mean particle size and the 90% cut-
off point showed a considerable increase. This means that the main change in the particle distribution occurred at the larger end of the distribution.

Table 3.5 gives the Malvern mean particle size results for the particular samples taken each day.

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<td>42.56</td>
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<td>42.56</td>
</tr>
</tbody>
</table>

Table 3.5: Malvern Particle Size Data from Stage 2

This data was analysed in great detail to investigate the trend in particle size throughout the gypsum formation step.
3.3.3.5 Analysis of Results

The data was initially analysed after 11 days and the conclusions drawn from this initial analysis were used in the subsequent data collection. A plot of mean particle size against sample points (numbered 1 to 11) illustrated the variation in mean particle size between the set of samples taken each day (see Figure 3.8).

![Figure 3.8: Plot of Mean Particle Size against Sample Points](image)

A plot of mean particle size for a particular sample against days illustrated how the mean particle size changed between samples over the period of days (see Figure 3.9).

![Figure 3.9: Plot of Mean Particle Size against Days](image)
Figure 3.10 illustrates the change in the percentage solids present in the wet samples based on 6 days analysis.

The results of the filterability tests are illustrated in Figure 3.11 while results of the analysis of potassium content in the sour filtrate are shown in Figure 3.12.
3.3.3.6 Discussion of Results

From Figure 3.8, a number of interesting observations were made. A significant decrease in mean particle size was evident from sample point no. 1 to 2 which suggested that attrition or crystal breakage was occurring between these points. The pump transferring the slurry from the final calcium citrate reaction vessel to the 1st stage calcium citrate filter, was thought to be the most likely cause of crystal breakage. Alternatives to the existing pumping mechanism was seen as a possible area of investigation, with a view to maintaining the crystal size obtained in the actual calcium citrate reaction. Improvements in the crystal size of the calcium citrate being filtered would in turn improve the calcium citrate filterability. A further slight decrease in mean particle size was then observed between the calcium citrate cake sampled from the first and second stage filters. This was probably due to the actual filtering mechanism but the break-up was not as significant here. Overlay plots of the Malvern results illustrate clearly the differences in particle size distributions between these three sample points (see Figure 3.13).

![Overlay Plot of Samples 1, 2, 3.](image)

The mean particle size was found to increase at the calcium citrate filter repulper stage, followed by a further slight increase at the vortex sample. No significant change was
observed from the vortex sample through to the gypsum filter feed tank samples, or the actual gypsum cake sampled from either the pannevis or the stand-by gypsum filter.

It was very evident that the trial without the vortex mixer (17/12/96) had a positive effect on the gypsum crystals. The mean particle size of the gypsum was found to increase from approximately 35-45μm with the vortex mixer, to approximately 60μm without the vortex mixer.

From this trial, an interesting observation with regard to the “tail” of the Malvern graph was made. Overlay plots of the crystal size distribution without the vortex mixer and distributions with the vortex mixer, suggested that no extra fines were produced when the vortex mixer was off line (see Figure 3.14). However, this appeared to contradict experiences on the plant as problems with fine hemihydrate gypsum were witnessed in the refining end during the trial.

![Figure 3.14: Overlay Plot of Sample No. 9 (with & without vortex mixer)](image)

Expectations of the Malvern graph were a wider size distribution, in particular a longer “tail”. The size distribution was found to be wider, but only on the large end of the scale. Further trials appeared necessary at this stage to clarify these findings. It seemed possible that changes in the crystal habit as opposed to the actual size were the problem, but verification of this required more analysis.
Figure 3.9 again highlighted the drop in particle size between the final calcium citrate reaction tank and the calcium citrate filtration step. The same general trend was also observed from the other sample points as in Figure 3.8. Although some changes were evident from day to day, the shape of the plot remained relatively constant which verified the variations between sample points.

A relatively conclusive trend was also observed from the solids data (Figure 3.10). The solids content in sample no. 1 was relatively low (35-45%) while that in sample no. 4 was almost twice as high. Dilution of the calcium citrate/gypsum slurry with sulphuric acid at the vortex mixer again reduced the solids content in samples 3 to 7. As expected, the solids measurement did not change significantly from the vortex sample to the filter feed tanks. The high solids content at the calcium citrate filter repulper seemed reasonable when consideration was given to the fact that slurry from the strike tank is recycled to the repulper where it is mixed with calcium citrate cake, thus increasing the quantity of solids.

The following observations were made from the data analysis for day 12 onwards. On comparison of the mean particle size results from the first gypsum filter feed tank over days 12 to 16, along with the previous trial without the vortex mixer (day 11), the mean particle size was seen to fluctuate between approximately 54\(\mu\)m and 66\(\mu\)m. Despite this fluctuation of results however, it was clearly evident that the mean particle size definitely increased when the vortex mixer was off-line (i.e. 40-45\(\mu\)m with vortex versus 54-66\(\mu\)m without vortex).

The particle size increase was verified visually through the microscopic analysis, and photograph records facilitated comparison with the crystals obtained when the vortex mixer was on-line (see Figures 3.15 and 3.16).

Results from the filterability test over the 5 days without the vortex mixer did not entirely support the theory that the larger the crystal size, the higher the filterability result. This was most probably due to the fact that the test was not carried out at the same temperature each day. The vacuum set-up used for the test was not always readily available because it was also being used for plant production tests which were a priority. Therefore in some cases, the
slurry was cooled somewhat prior to testing, yielding a lower filterability result (see Section 4.5 for filterability - temperature relationship).

A number of calcium citrate assays were carried out to investigate the quantity of calcium citrate in various samples. Results from the calcium citrate filter repulper sample suggested the presence of approximately 25% calcium citrate. This amount of calcium citrate was expected, considering a mass balance around this area (see Section 3.4). The analysis performed here quantified previous observations that the quantity of calcium citrate in this sample appeared quite small in comparison to the amount of gypsum evident in the microscopic analysis. As the microscopic analysis is very subjective however, the calcium citrate assay result was taken as correct. Therefore, any previous suspicions regarding the occurrences at the filter repulper stage were eliminated.

Calcium citrate assays were also carried out on samples from the strike and trim tanks and the first gypsum filter feed tank, to investigate the quantities of calcium citrate present at the various reaction stages. A small quantity of calcium citrate was found present in the strike tank sample (1.5-2.8%) which agreed with the fact that most of the calcium citrate should be
decomposed at this stage, allowing the trim tank to complete the reaction. Contrary to expectations however, approximately 0.5% calcium citrate was still found in the filter feed tank. As the calcium citrate should be fully decomposed at this stage, no calcium citrate was expected in this sample.

Theoretically, if the pH of the sour filtrate at a specific gravity of 1116 is 1.05 or less, there should be no calcium citrate left in the filter feed tank. The pH measurements at the time of analysis yielded results of less than 1.05 (i.e. 0.98/0.99) suggesting that the calcium citrate assay results contradicted the theoretical possibilities. The only explanation possible at this stage was the presence of calcium citrate 'grit' in the filter feed tank which was dumped in at the calcium citrate filter repulper. This calcium citrate grit is difficult to decompose to form gypsum, which would explain the presence of calcium citrate in the gypsum filter feed tank. A laboratory reaction carried out at a later stage with a significant quantity of calcium citrate grit in the reactant slurry, showed that the grit was not fully decomposed even with excess H$_2$SO$_4$.

On examination of the sour filtrate, the total amount of solids present did not really change between operation with and without the vortex mixer. However, as expected, the percentage of hemihydrate gypsum (grey layer) was smaller when the vortex mixer was on line.
3.3.3.7 Conclusions From Database

The microscopic analysis and photograph records of the samples proved to be successful in illustrating the differences in crystals from sample to sample. Although this analysis is very subjective, a satisfactory amount of information was identified and the particular crystal habits of both the calcium citrate and gypsum were easily observed. The gypsum habit appeared to be highly twinned while the calcium citrate crystals were flat rectangular plates. The increase in size of the gypsum crystals without the vortex was very obvious from the photographs.

The Malvern analysis highlighted the trends and variations between the samples and facilitated the identification of areas of most significance with regard to changes in crystal size.

The filterability test of the trials without the vortex mixer highlighted the influence of increased particle size on the filterability [Range: 630-940 ml/min. (with vortex) versus 750-1200 ml/min. (without vortex)]. An increase in the quantity of hemihydrate in the filtrate without the vortex mixer, was also confirmed.

Analysis of the amount of potassium in the sour filtrate yielded very good results throughout the data collection [Range: 28 - 74 ppm K/HCA]. This implied that the calcium citrate filtration mechanism was operating very well, i.e. most of the potassium was removed at this stage.

Monitoring of various parameters in the plant did not lead to any satisfactory conclusions with regard to their influence on the crystal characteristics because the variation in these parameters from day to day was too significant to allow any conclusive trends to be determined.
3.4 Mass Balance Around Gypsum Reaction Step

3.4.1 Overall Balance

A mass balance was carried out around the gypsum reaction step. Figure 3.17 shows a block diagram which illustrates the area around which the overall mass balance was performed.

![Figure 3.17: Block Diagram of Gypsum Reaction Step](image)

The gypsum reaction is written as:

\[
\text{Calc. Citrate} + \text{H}_2\text{SO}_4 + 2\text{H}_2\text{O} \rightarrow \text{C}_6\text{H}_8\text{O}_7\cdot\text{H}_2\text{O} + \text{CaSO}_4\cdot2\text{H}_2\text{O} \quad \text{.........}(3.1)
\]

The calcium citrate flowrate, recycle flowrate and the sulphuric acid flowrates to the strike and trim tank were recorded from the plant control room (streams 1, 3, 4 and 6 respectively). Samples were taken from the plant to represent each stream as illustrated in Figure 3.17 and the density of each sample was measured. The data obtained is given in Table 3.6.

<table>
<thead>
<tr>
<th>Calcium Citrate Flowrate</th>
<th>290 GPM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Recycle Flowrate</td>
<td>240 GPM</td>
</tr>
<tr>
<td>Sulphuric Flowrate to Strike</td>
<td>8 GPM</td>
</tr>
<tr>
<td>Sulphuric Flowrate to Trim</td>
<td>0.33 GPM</td>
</tr>
<tr>
<td>Density Stream 1</td>
<td>1.112 g/cm³</td>
</tr>
<tr>
<td>Density Stream 2</td>
<td>1.300 g/cm³</td>
</tr>
<tr>
<td>Density Stream 3</td>
<td>1.348 g/cm³</td>
</tr>
<tr>
<td>Density Stream 5</td>
<td>1.333 g/cm³</td>
</tr>
<tr>
<td>Density Stream 7</td>
<td>1.367 g/cm³</td>
</tr>
</tbody>
</table>

Table 3.6: Data for Mass Balance
Stream 1
Calcium citrate flowrate = 290 GPM
1 Gallon = 4.546 litres
⇒ 290 GPM = 1318.34 l/min. = 1.31834 m³/min.
Density, \( \rho = 1112 \text{ kg/m}^3 \)
⇒ Calcium citrate mass flowrate = (1.31834 m³/min.) x (1112 kg/m³) = 1465.99 kg/min.
Approximately 40% of this stream is solids
⇒ Mass flowrate of solids = (0.4) x (1465.99 kg/min.) = 586.4 kg/min
Assuming 45% of this is moisture,
⇒ Actual solids mass flowrate = (0.55) x (586.4 kg/min.) = 322.52 kg/min.
⇒ Stream 1 = 322.52 kg/min.

Stream 4
Sulphuric acid flowrate to strike tank = 8.5 GPM = 38.641 l/min. = 0.038641 m³/min.
Density, \( \rho = 1835 \text{ kg/m}^3 \)
⇒ Sulphuric acid mass flowrate = (0.038641 m³/min.) x (1835 kg/m³) = 70.9 kg/min.
⇒ Stream 4 = 70.9 kg/min.

Stream 6
Sulphuric acid flowrate to trim tank = 0.33 GPM = 1.5 l/min. = 0.0015 m³/min.
Density, \( \rho = 1835 \text{ kg/m}^3 \)
⇒ Sulphuric acid mass flowrate = (0.0015 m³/min.) x (1835 kg/m³) = 2.75 kg/min.
⇒ Stream 6 = 2.75 kg/min.

Stream 7
From Figure 3.16, Stream 7 = Stream 1 + Stream 4 + Stream 6
⇒ Stream 7 = 322.52 kg/min. + 70.9 kg/min. + 2.75 kg/min. = 396.176 kg/min.
⇒ Stream 7 = 396.176 kg/min.
Density \( \rho = 1367 \text{ kg/m}^3 \) ⇒ Stream 7 = 0.2898 m³/min. = 289.8 l/min. = 63.75 GPM
This flowrate of 63.75 GPM corresponded to the recorded plant flowrate of 64 GPM.
**Stream 5**

From Figure 3.16, Stream 5 + Stream 6 = Stream 7

\[ \Rightarrow \text{Stream 5} = 396.176 \text{ kg/min.} - 2.75 \text{ kg/min.} = 393.43 \text{ kg/min.} \]

\[ \Rightarrow \text{Stream 5} = 393.43 \text{ kg/min.} \]

Density \( \rho = 1333 \text{ kg/m}^3 \) \( \Rightarrow \text{Stream 5} = 0.295 \text{ m}^3/\text{min.} = 295 \text{ l/min.} = 64.9 \text{ GPM} \)

This flowrate of 64.9 GPM corresponded to the recorded plant flowrate of 64 GPM.

**Stream 3**

Recycle Flowrate from Strike Tank to Calcium citrate Filters = 240 GPM

\[ \Rightarrow \text{Recycle Flowrate} = 1091.04 \text{ l/min.} = 1.091 \text{ m}^3/\text{min.} \]

Density, \( \rho = 1348 \text{ kg/m}^3 \)

\[ \Rightarrow \text{Recycle mass flowrate} = (1.091 \text{ m}^3/\text{min.}) \times (1348 \text{ kg/m}^3) = 1470.7 \text{ kg/min.} \]

\[ \Rightarrow \text{Stream 3} = 1470.7 \text{ kg/min.} \]

**Stream 2**

From Figure 3.16, Stream 2 = Stream 1 + Stream 3

\[ \Rightarrow \text{Stream 2} = 322.52 \text{ kg/min.} + 1470.7 \text{ kg/min.} = 1793.22 \text{ kg/min.} \]

\[ \Rightarrow \text{Stream 2} = 1793.22 \text{ kg/min.} \]

**Overall Balance Around Strike Tank**

From Figure 3.19, Stream 2 + Stream 4 = Stream 3 + Stream 5

\[ \Rightarrow 1793.22 \text{ kg/min.} + 70.9 \text{ kg/min.} = 1470.7 \text{ kg/min.} + 393.43 \text{ kg/min.} \]

\[ \Rightarrow 1864.12 \text{ kg/min.} = 1864.13 \text{ kg/min.} \]
Stream 1 = 322.52 kg/min. (total)

This stream is made up of approximately 45% moisture and 55% calcium citrate

⇒ Calcium citrate = 177.386 kg/min., ⇒ Water = 145.134 kg/min.

The components of stream 7 are calculated using the gypsum reaction equation as follows:

\[
\text{Calc. Citrate + H}_2\text{SO}_4 + 2\text{H}_2\text{O} \rightarrow \text{C}_6\text{H}_8\text{O}_7\cdot\text{H}_2\text{O} + \text{CaSO}_4 \cdot 2\text{H}_2\text{O}
\]

\[
\begin{array}{cccc}
\text{Calc. Citrate} & \text{H}_2\text{SO}_4 & \text{H}_2\text{O} & \text{CaSO}_4 \cdot 2\text{H}_2\text{O} \\
177.386 & 177.386 & 177.386 & 123.026 \\
\end{array}
\]

- **Citric Acid** produced = 177.386 kg/min. x (210 / 248) = 150.206 kg/min.
- **Gypsum** produced = 177.386 kg/min. x (172 / 248) = 139.956 kg/min.
- **Sulphuric Acid** used = 177.386 kg/min. x (98 / 248) = 70.096 kg/min.
- **Water** used = 177.386 kg/min. x (26 / 248) = 25.75 kg/min.

The component balance is summarised in Table 3.7. It is evident that the total sum of streams 1, 4 and 6 is equal to the total of stream 7 as expected.

<table>
<thead>
<tr>
<th>Component</th>
<th>1</th>
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<th>7</th>
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<td></td>
<td>119.384</td>
</tr>
<tr>
<td>H₂O</td>
<td>145.134</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>CaSO₄·H₂O</td>
<td></td>
<td></td>
<td></td>
<td>123.026</td>
</tr>
<tr>
<td>C₆H₈O₇·H₂O</td>
<td></td>
<td></td>
<td></td>
<td>150.206</td>
</tr>
<tr>
<td>H₂SO₄</td>
<td>70.9</td>
<td>2.75</td>
<td>3.554</td>
<td></td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td>322.52</td>
<td>70.9</td>
<td>2.75</td>
<td>396.17</td>
</tr>
</tbody>
</table>

Table 3.7: Component Balance Summary
Chapter Four

Laboratory Analysis
4.1 Introduction

This chapter details the laboratory tests and analytical methods used throughout the project. The following tests and analytical methods were used:

- Malvern Particle Size Measurement
- Microscopic Analysis
- Filterability Test
- Flame Photometry
- Solids Test
- Calcium Citrate Assay
- Atomic Absorption

In this chapter, each test and analytical method is described in context of the application to the project. Particular emphasis is placed on the measurement of particle size since this formed an integral part to the entire project development. All of the above tests and methods were found to be successful in their applications during the project.

4.2 Particulate Processes and Particle Size Distribution

The particulate nature of solids is characterized by form and size, as opposed to liquids or gases, which assume the shape of the volume within which they are contained. Crystallization processes yield products of a particulate nature. The particles are characterized by both a size and representative shape. As no two particles will be exactly the same size, the material must be characterized by the distribution of sizes or particle size distribution. In the case of a crystallization or precipitation process, the distribution of sizes is known as the crystal size distribution.

The particle size distribution of a solid material is important in the end-use applications of the material, e.g. filtration rate. In general, uniformly sized particles are easier to handle, filter, and dewater, and hence are more desirable. Particle technology is a term used to describe the overall external shape and appearance of particulate solid. More specifically, crystal morphology and habit describe the shape and appearance of crystalline materials (see Section 2.2.5). Crystal morphology and crystal habit are well-defined terms that
respectively describe the appearance of faceted (flat surfaced) crystals due to the specific crystallographic faces showing, versus the crystal shape given by the relative length to width of the crystal faces. The Miller indices of the different crystal faces showing give the crystal morphology. Heywood, (1968) defined particle shape or crystal habit as being:

- Acicular: Needle shaped
- Angular: Sharp-edged with a roughly polyhedral shape
- Dendritic: A branched, crystalline shape
- Fibrous: Thread-like
- Flaky: Plate-like
- Granular: Irregular but of approximately spherical overall form
- Irregular: Lacking any symmetry
- Modular: A rounded, irregular shape

These terms are useful rough guides but most theories of particle size are based on assumptions to a regular shape. Theoretical calculations are based on certain shapes, usually spheres. Only certain morphologies (crystal faces showing) are possible for any crystal system (molecular lattice structure), but both morphology and habit depend on the growth conditions and can vary with the level of supersaturation.

A particle may be thought of as the element of matter that best describes the state of subdivision of the material and has a shape characteristic of the processes and forces producing the particles (Irani and Callis, 1963). With this definition of a particle, then particle size must be the linear dimension that best characterizes the state of subdivision of the material within the context of the typical shape of the particles. A characteristic dimension of a particle can be thought of as a line passing through the centre of mass of the particle and intersecting two opposing surfaces. For highly irregular particles, such characteristic sizes are infinite in number and can be represented by a one-dimensional frequency distribution. This variation in characterization of individual sizes is averaged when a size distribution is obtained on a sample containing a large number of particles.

Miller Indices - A method of relating crystal faces to internal structures by defining the intercept of each crystal face with the crystal axes.
The actual size that is measured in a particle size distribution analysis, lies between the minimum and maximum characteristic sizes and depends on the method of measurement. It is essential to note that no definition of particle size is complete without specifying the technique of size measurement.

4.3 Malvern Particle Size Measurement

The size measurement technique used for this project was the Malvern particle size analysis method using the Malvern Mastersizer. This method offers a number of advantages.

- The method is an absolute method set in fundamental scientific principles, hence there is no need to calibrate the instrument against a standard.
- A wide dynamic size range can be measured (0.05 - 3500μm typically).
- Sample presentation is straightforward using an easy-to-handle measurement cell.
- Liquid suspensions can be measured in a recirculating cell and this gives high reproducibility.
- Although the samples are small and a representative sample must be obtained, the entire sample passes through the laser beam and diffraction is obtained from all the particles.
- The method is non-intrusive using a low power laser beam to probe the particle size.
- The method is rapid and produces a volume distribution in less than one minute. This means rapid feedback to the operating plant and repeat analyses are made very easily.
- The Malvern particle size measurement is a highly reproducible technique which means that the results can be relied on. Therefore, genuine product changes can be readily detected.
- A high resolution size discrimination is given and up to 100 size bands can be displayed.

The Mastersizer system consists of four basic components:

1. Optical measurement unit
2. Sampling handling accessories
3. Computer system
4. Malvern operating software
The optical measurement unit is the main measurement facility for the system. This basically provides a collimated laser that passes through the sample to be measured. The scattered laser light from the sample is detected by the receiver of the optical measurement unit. This data from the receiver is transmitted to the computer system where the Malvern operating software calculates the size distribution. Figure 4.1 shows a photograph of the Malvern Mastersizer instrument in place at ADM Ringaskiddy.

![Figure 4.1: Malvern Mastersizer Instrument at ADM Ringaskiddy](image)

In order to understand the meaning of results reported by the Malvern diffraction instrument, there are a number of fundamental concepts which require explanation.

- **The result is volume based.** The size distribution derived by this technique is volume based. This means that if the result indicates that 43% of the sample is below 120μm, then the total volume of all the particles with diameters less than 120μm in size is 43% and therefore, 57% of the total volume of sample is greater than 120μm.

- **Derived distribution parameters.** The analysed distribution is expressed in a set of size classes which are optimised to match the detector geometry and optical configuration giving the best resolution. All parameters are derived from this fundamental distribution. Distribution parameters and derived diameters are calculated from the fundamental distribution using the summation of the contributions from each size band. The representative diameter for each band is taken to be the
geometric mean of the size band limits: $\sqrt{d_{i-1}d_i}$. This number will be slightly different to the arithmetic mean: $\frac{1}{2}(d_{i-1} + d_i)$. The geometric mean is chosen in preference to the arithmetic mean as it is more appropriate to the logarithmic spacing of the fundamental size classes. The same principle of calculation applies to the distribution statistics standard deviation, skewness and kurtosis. For "mono-size" distributions, the distribution mean is reported as the geometric mean of the size class and standard deviation, skewness and kurtosis are reported as zero. Creation of a spline fit to the fundamental result is the procedure used for other parameters of the distribution. Intermediate values are then read off this curve allowing interpolation of percentile points which do not coincide with the measurement size band boundaries.

• **The result is expressed in terms of equivalent spheres.**

A cylindrical particle of diameter 20µm and length 60µm has a volume, V.

$$V = \pi (10\mu m)^2 (60\mu m) \quad \text{(4.1)}$$

The sphere of equivalent volume would have a diameter centred on:

$$\sqrt[3]{\frac{6V}{\pi}} = 33\mu m \quad \text{(4.2)}$$

with a spread from 20 to 60µm.

Sieving would pass the particles through a 20µm aperture and classify them as 20µm, while the Malvern Mastersizer would classify the particle as being 33µm.
4.3.1 Data and Results

Data, Sample and Background

The output of the measurement is arrays of values containing the results of the background and sample measurements. The background measurement must be subtracted from the sample measurement to get the actual scattering from the sample particles alone. A correction must be used in the subtraction of the background measurement from the sample measurement. The corrected background subtraction can be expressed as:

\[ D_j = S_j - (1 - Ob)B_j \] ...................(4.3)

where,
\[ D \] is the data
\[ j \] is the channel number
\[ S \] is the sample measurement
\[ B \] is the background measurement
\[ Ob \] is the obscuration, defined as: \( Ob = 1 - \frac{L_s}{L_b} \)

\( L_s \) is the light intensity measured in the central detector when a sample is present in the cell, \( L_b \) is the same but with clean dispersant, i.e. no sample.

Analysis, Residual and Data Fit

Analysis is the point at which the measured data and the additional experimental parameters are processed to give the result. The technique used is that of constrained least squares minimisation in an iterative process. The comparison of calculated and measured data is by least squares error and the user is able to inspect both sets of data and the least squares error (expressed as a residual). The analysis calculates the relative volume distribution as its fundamental result. All other results are based on this distribution. The concentration is determined from the laser beam obscuration, knowing this distribution and the beam length parameter. All other output information is derived from these results by use of numerical manipulation assuming spherical particles.

The residual value is connected with the result quality. If a residual of < 0.3% is obtained, the data fit is very good. A residual of 0.3 to 1% means a good fit, while a residual over 1% is poor. If a residual of greater than 1% is obtained, the analysis should be repeated.
4.3.2 Derived Diameters and Distribution Statistics

The result from the analysis is the relative distribution of volume of particles in the range of size classes. From this basic result, the statistics of the distribution are calculated. Figure 4.2 shows examples of the result graph types. The result is also interpolated so the result at points in-between the size class boundaries is available. The cumulative undersize and oversize, frequency curves and histograms are obtained from the interpolated result. The frequency curve is obtained by differentiation of the cumulative undersize curve. The peak of the frequency curve gives the modal diameter - the most commonly occurring particle diameter.

The statistics of the distribution are calculated from the raw result using the derived diameters $D_{m,n}$ - an internationally agreed method of defining the mean and other moments of particle size. The derived diameters are defined:

$$D_{m,n} = \left[ \frac{\sum V_i d_i^{m-3}}{\sum V_i d_i^{n-3}} \right]^{1/\left(m-n\right)}$$

(4.4)

where, $V_i$ is the relative volume in class $i$ with mean class diameter of $d_i$, $m$ and $n$ are integer values which describe the type of derived diameter.

Some well known examples of derived diameters are:

$D[4,3]$ This is the volume mean diameter. It is the diameter of the sphere having the same volume as the real particle.

$D[3,2]$ This is the surface area mean diameter or sauter mean diameter. It is the diameter of the sphere having the same surface area as the real particle.
The interpolated results allow the cumulative undersize result to be determined for any size, or the size can be determined for any percent of the total result under that size. This is known as a percentile. Some examples of percentiles are as follows:

\( D[v, 0.1] \) The 10% volume percentile (10% of the distribution is below this value).

\( D[v, 0.9] \) The 90% volume percentile (90% of the distribution is below this value).

\( D[v, 0.5] \) The 50% volume percentile, also known as the \textit{volume median diameter}. 50% of the distribution is above and 50% below this value - it divides the distribution exactly in half. It must not be confused with the mean diameter, \( D[4,3] \).

### 4.3.3 Stages of the Measurement

The stages of the measurement are best described using a diagram, (see Figure 4.3).

![Figure 4.3: Measurement Stages](image)
Chapter Four - Laboratory Analysis

The following procedure was used for each measurement of particle size:

A file was opened to save the results of the measurements. The analysis model and presentation were set. The particle handling system and cell were cleaned and the sample dispersion unit was filled with fresh isopropyl alcohol. Documentation of the sample was entered - a short sample identifier and any notes to be saved or printed with the result.

The automatic alignment procedure was started. This centred the detector on the laser beam. The light scattered from the clean dispersant was measured. This was a two stage process. The first stage was to measure the electrical offset of the detector amplifiers which was then subtracted from all subsequent measurements. The second stage measured the scattering with no sample in the dispersant. The sample was added dropwise to the dispersant in the dispersion tank. The scattering from the sample was measured to create the data. The data was analysed to form a result - the relative distribution of particle volume with size. The measurement and result was saved as a record in the sample file.

The result was printed with several options available for the information to be included in the print (see Section 4.3.4). The particle handling system was cleaned by passing fresh dispersant through it until all the sample was removed. If the system was not cleaned sufficiently by flushing, it meant that there were particles attached to the cell windows. The windows then had to be removed and cleaned.

4.3.4 Viewing Results

The data and results produced by the Malvern Mastersizer are presented in the forms of tables and graphs on screen or printed report. Although a series of options were available for the result table and report format, the result formats most frequently used in this project were:

- **Analysis Result Report** - reports the calculated size distribution as in-band, under-size or over-size distributions. A number of distribution characteristics derived from the distribution results are also displayed.

- **Histogram Result Report** - same information as in Analysis Report except that the listed distribution result is classified in the user defined size bands.
• *Sieve Result Report* - displays the analysis result classified on standard sieve aperture diameters.

A copy of each of these report formats for a single sample is given in Appendix B.

### 4.3.5 Reproducibility of Malvern Results

In order to experimentally verify the reproducibility of the Malvern results, one sample was analysed five times consecutively. The mean particle size, 90% and 10% percentile points obtained are given in Table 4.1 below:

<table>
<thead>
<tr>
<th>Measurement</th>
<th>D(v, 0.5) (microns)</th>
<th>D(v, 0.9) (microns)</th>
<th>D(v, 0.1) (microns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>41.18</td>
<td>81.56</td>
<td>11.75</td>
</tr>
<tr>
<td>2</td>
<td>41.16</td>
<td>81.01</td>
<td>11.77</td>
</tr>
<tr>
<td>3</td>
<td>41.17</td>
<td>82.64</td>
<td>11.86</td>
</tr>
<tr>
<td>4</td>
<td>41.56</td>
<td>81.72</td>
<td>11.79</td>
</tr>
<tr>
<td>5</td>
<td>41.92</td>
<td>82.15</td>
<td>12.01</td>
</tr>
</tbody>
</table>

**Table 4.1: Malvern Result Reproducibility**

A plot of the data given in Table 4.1 is shown in Figure 4.4.

![Figure 4.4: Malvern Result Reproducibility](image)

The graph in Figure 4.4 clearly illustrates that no significant change occurs between measurements of the same sample. This was verified mathematically by calculation of the
mean and standard deviation of the mean particle size of the five measurements. The mean was found to be 41.478μm with a standard deviation of 0.316. An overlay plot of the Malvern distributions also verified that the results were reproduced over the five measurements.

As discussed in Section 4.3.1, the residual value obtained for each measurement was also important in determining the validity of the result. Therefore, knowing that the Malvern results were reproducible (as proved experimentally), and by ensuring that the residual value obtained for each measurement was less than 1%, the Malvern Mastersizer was used for all the laboratory experiments to produce reliable results.

### 4.4 Microscopic Analysis

Although the Malvern Mastersizer provided a significant amount of information about the size distribution of a particular sample, analysis of the sample using a microscope was necessary to form a physical image of the actual crystal type present. Figure 4.5 is a photograph of the microscope and camera used during the project work at ADM.

This microscopic technique was useful as it allowed one to look directly at the particles. The shape of the particles was seen and it was also used to determine the presence of agglomeration in the system. Since this analysis can be subjective, it was used in conjunction with the Malvern analysis for the duration of the project to obtain a physical representation of the sample material. A photograph record was made of each sample analysed to facilitate comparison of the crystal types over a series of days or experiments.
Figure 4.6 below shows the microscopic analysis of a typical calcium citrate sample taken from the second stage calcium citrate filter and Figure 4.7 represents a typical gypsum sample taken from the trim tank.

The corresponding Malvern analysis for these samples is given in Appendix C. The mean particle size of the calcium citrate crystals was found to be 30.28\(\mu m\) with 10% of the distribution greater than 66.39\(\mu m\) and 10% smaller than 8.46\(\mu m\). The mean particle size of the gypsum crystals was found to be 54.89\(\mu m\) with 10% of the distribution greater than 110.42\(\mu m\) and 10% smaller than 14.44\(\mu m\).

4.5 Filterability Test

Due to the influence of the gypsum filtration rate on ADM’s citric acid production rate, measurement of the filterability of the samples formed an integral part of the laboratory analysis. The procedure used to measure the filtration rate was as follows:
Procedure:

- A Buchner flask was set up for vacuum filtration at a vacuum pressure of approximately 0.5 bar.
- The filter cloth used was 1746 PES which corresponded to that used on the plant Pannevis filter.
- 500 ml of sample was poured onto the filter cloth.
- The timer was started when the first drop of slurry met the filter and stopped when the last drop of liquid disappeared from the cake. Results were reported in ml/min.

Precaution:
For reproducible results, the samples were at the same temperature for each test. This was necessary due to the temperature dependence of the filtration rate. The results obtained from filtering a sample at four different temperatures are given in Table 4.2. A graphical analysis of the results is illustrated in Figure 4.8.

<table>
<thead>
<tr>
<th>Temp. (deg. C)</th>
<th>Time (secs.)</th>
<th>Filterability (ml/min.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>67</td>
<td>52</td>
<td>577</td>
</tr>
<tr>
<td>55</td>
<td>61</td>
<td>492</td>
</tr>
<tr>
<td>46</td>
<td>72</td>
<td>417</td>
</tr>
<tr>
<td>36</td>
<td>77</td>
<td>390</td>
</tr>
</tbody>
</table>

Table 4.2: Filterability Results

Figure 4.8 clearly illustrates that the filtration rate deteriorated as the sample cooled. Hence, it was necessary to perform tests for comparison at the same temperature.

4.6 Flame Photometry

During the database development described in Chapter 3, the amount of potassium present in the sour filtrate was measured using flame photometry. This was to determine how well the plant calcium citrate filters were operating. A high potassium content indicated poor filtration while a low content indicated good filtration. The procedure used is described below:
**Procedure:**

- Approximately 5 grams of the filtrate retained from the filterability test was taken and diluted with distilled water to about 150 mls. in a conical flask.
- This solution was titrated with 1N NaOH using a few drops of phenolphthalein indicator. The end-point was reached when a permanent pink colour was reached.
- The titre obtained was used to determine the % w/w Hydrous Citric Acid (HCA).
- An additional 5 grams of the filtrate was diluted to 100 mls. in a volumetric flask using distilled water. (This mass of filtrate had to be increased or decreased, depending on the reading obtained when using the flame photometer).
- The flame photometer was set up for potassium (K) analysis and blanked using distilled water.
- A 10 ppm K standard was then used to measure 100% reading on the instrument.
- This procedure was repeated until the readings obtained for the blank and the standard were consistent and correct.
- The filtrate solution was then analysed and the level of K present determined, the result reported in ppm.

The operating status of the calcium citrate filters was determined using an index guide:

| < 100 ppm | Very Good |
| 100 - 300 ppm | Good |
| 300 - 400 ppm | Fair |
| 400 - 600 ppm | Poor |
| > 600 ppm | Bad |

**4.7 Solids Test**

The percentage of solid material in the slurry samples as well as the solids content in the sour filtrate was determined using the solids test. This involved spinning 10ml of sample in a centrifuge for approximately 15 minutes. At the end of the 15 minutes, the percentage of solids was determined using the graduations on the cuvettes. Although this measurement was only approximate, it gave a good indication of the difference in solids content between the various slurry samples. The amount of solids in the filtrate samples was usually less than 0.5% but the layers of solid material present were still quite...
distinguishable. This measurement was particularly used to monitor the amount of hemihydrate gypsum in the filtrate from the gypsum step.

4.8 Calcium Citrate Assay

The amount of calcium citrate in a particular sample was determined by carrying out a calcium citrate assay. This analysis was used to monitor the conversion of calcium citrate to gypsum during the gypsum formation. The procedure used is described below:

Procedure:

- Calcium citrate slurry was filtered using the filtration apparatus for the filterability test (see Section 4.5).
- The filter cake was washed repeatedly with cold water until all traces of citric acid were removed from the cake. The presence of remaining citric acid was checked at intervals during the washing stage by titrating the wash water with 0.1N NaOH (using phenolphthalein indicator). When a permanent pink colour was achieved by a single drop of NaOH, the washing was complete.
- The calcium citrate cake was then washed with acetone and dried in an oven.
- 1 gram of the dried calcium citrate cake was weighed.
- Approximately 150 mls. of distilled water were added to the cake in a conical flask.
- A few drops of phenolphthalein indicator were added and heated to boiling using a magnetic pellet to agitate the solution.
- The solution was titrated with 0.1N NaOH. The end-point was reached when a permanent pink colour was achieved.

Precautions:

- Care was taken when reaching the end-point because the solution turned pink and appeared to have been neutralized, however on boiling for a while, the pink colour disappeared. More NaOH was then required to reach the actual end-point.
- Only cold water was used to wash the calcium citrate cake because the cake is soluble in warm / hot water.
4.9 Atomic Absorption

Atomic Absorption was used during the laboratory experimental trials (see Chapter 6) to determine the quantity of impurity present in a particular sample. The plant samples were analysed to quantify the presence of a particular impurity. In the laboratory experimental trials, various quantities of impurities were added to the reaction mixture to investigate their influence on the gypsum crystals and their filtration rate. The presence of the impurities remaining in the filtrate after filtration was determined using this well-known analysis technique.

4.10 Discussion

The laboratory tests and analytical methods described in this chapter were used throughout the project to develop the plant database (Chapter 3) and also to analyse the experimental work described in Chapter 6.

The Malvern particle size measurement provided detailed crystal size distributions which were necessary to quantify the crystal variations during the project. The microscopic analysis formed a visual representation of the actual crystalline materials. This analysis, used in conjunction with the Malvern Mastersizer, provided all the particle data required for the project. The filterability test was adequate to measure the slurry filtration rates. The solids test provided a measurement of the solids content in the slurry samples and also facilitated qualification of the solid material remaining in the filtrates. The calcium citrate assays gave successful measurements of the degree of conversion of calcium citrate to gypsum. Flame photometry was used to determine the quality of the calcium citrate filtration step in the plant, while atomic absorption was used to quantify the impurities in various samples. All of the analytical techniques described in this chapter were used as applicable and were therefore successful in their production of results for this project.
Chapter Five

Design and Set-Up of Laboratory Rig
5.1 Introduction

This chapter describes the design and set-up of the experimental laboratory rig. Details of the equipment chosen and an overall description of the rig is given. A safety report is included which highlights the safety considerations taken during the initial set-up as well as during the actual operation within the laboratory. The laboratory environment, equipment and apparatus assembly safety features, materials safety data, personal protection and waste disposal are all addressed. A hazop study which provided detailed assessment of the potential hazards associated with the operation of the experimental rig is also included. The problems encountered during the laboratory trials are discussed and the steps taken to overcome the difficulties are also outlined.

5.2 Experimental Rig Design Considerations

From the plant studies outlined in chapter 3, it was evident that due to continuous fluctuations in the plant operating conditions, detailed evaluation of the gypsum reaction step could not be achieved from the plant study alone. A laboratory experimental rig was therefore designed and set-up to facilitate characterisation of the gypsum formation reaction.

The design was based on the desire to initially reproduce the plant results using a laboratory rig, and then progress to intensive experimental trials to investigate the possible improvements available for the gypsum formation reaction and filtration steps. It was decided to use a single reactor to mimic the strike and trim tanks on the plant, in order to facilitate easier control of the reaction conditions. The temperature and pH of the reaction mixture were the main reaction control parameters, while the reactant flowrates also needed to be considered. Due to the dangerous properties of sulphuric acid (96% w/w), the method of sulphuric acid addition to the reactor was an important issue. In addition, proper dispersion of the acid into the reactor slurry was crucial for the formation of the desired dihydrate gypsum crystals.
5.3 Choice of Equipment

Prior to the commencement of experimental trials, the experimental laboratory had to be totally equipped. Although some equipment was already available at ADM, much of the required apparatus had to be purchased. A photograph of the laboratory set-up is shown in Figure 5.1 while a schematic of the experimental apparatus is given in Figure 5.2.

Due to the corrosive nature of the reaction substances, 316L stainless steel was the material of construction chosen for any material in contact with these substances. A 6.5 litre cylindrical vessel was constructed for the main reaction vessel which acted as both a reactor and a crystallizer. An axial flow impeller was used to agitate the reactor contents. Agitation was achieved by the use of an axial flow impeller. A Heidolph RZR1 stirrer motor was used to drive the agitator. A Haake DC5-W46/B open water bath circulator was chosen for temperature control of the reactor. The selection of this model was based on the working temperature range, the temperature accuracy required and the dimensions of the reactor. The reactor was immersed in the water bath which controlled the reactor temperature to an accuracy of +/- 0.01K. An Orion 720A pH meter was used to control the reaction and a temperature probe was also used in conjunction with this meter for temperature compensation. The pH and temperature of the reaction mixture could therefore be monitored at all times.
Watson-Marlow (504S/RL and 504U/RL) peristaltic pumps were purchased for the transfer of reactants to the reactor and also for sampling from the reactor. The pump models and pump-heads chosen were based on the desired flowrates (see Appendix D for pump calibration details). Silicone tubing (4.8mm) was used with the slurry pumps while Viton tubing (3.2mm) was used with the sulphuric acid feed pump.

A stainless steel dip-tube attached to the Viton tubing was used to disperse the sulphuric acid into the reactor. A 90\(^\circ\) bend towards the end of the tube facilitated dispersion of the acid through three needle-sized holes in the end section of the tube. The dip-tube was positioned just over the impeller to ensure adequate dispersion and mixing of the acid throughout the reactor.

A Stuart SH4 hot-plate was purchased to heat the reactant slurry prior to addition to the reactor. An agitator, again driven by a Heidolph RZR1 stirrer motor was used to maintain the reactant slurry solids in suspension. Additional general laboratory equipment, glassware and sampling equipment was also purchased for use during the trial work.

### 5.4 Laboratory Safety Report

#### 5.4.1 Environment

Prior to the commencement of any experimental work, the laboratory environment was examined from a safety viewpoint.

- All electrical sockets were linked to a junction box with suitable trip switches.
- An overall mains isolation switch was in an accessible location for use in an emergency situation.
- The laboratory was equipped with appropriate fire equipment (foam spray and carbon dioxide fire extinguishers and a fire blanket).
- An extraction fan was located on the wall behind the experimental apparatus and the other three walls had windows which could be used for ventilation if necessary.
5.4.2 Equipment Safety Features

Water Bath

The water bath system fulfilled the requirements of safety class 2 according to DIN 12879 and was therefore suitable for unsupervised continuous operation. (Safety Class 2: A variably adjustable excess temperature protection and independent low liquid level protection which is pre-set to the lowest level, allow the usage of different heat transfer liquids).

The comprehensive safety system was designed on the principle of the concept of the “single fault” which assumes that two separate faults do not occur simultaneously. The system therefore offers protection against one (single) fault. Such faults included:

- Fault in the temperature control unit:
  ⇒ Excess temperature  ⇒ Possible fire danger

- Leakage in the liquid circuit, or evaporation of heat transfer liquid:
  ⇒ Low liquid level  ⇒ Possible fire danger

- Pump blocked, or heat transfer liquid too highly viscous:
  ⇒ Motor overheating  ⇒ Possible fire danger

- Excess temperature protection level set incorrectly:
  ⇒ Possible fire danger

If a safety feature was triggered:

- A Fault Identification System (FIS) and an acoustic signal indicated the fault.
- The safety-relevant components of the heating unit (heating element and motor) were switched off immediately, i.e. the safety circuit transferred the unit to a stable, safe condition.
- The heat transfer liquid in the heating unit gradually adjusted to ambient temperature.

The following fault displays were possible for the water bath:

\[ AL^{\circ}C = Excess\ temperature \]

**Cause:** Excess temperature set too closely to the desired working temperature  
**Action:** Increase value slightly

**Cause:** The control function is defective  
**Action:** Return unit for servicing
**AL -n = Low liquid level**

**Cause:** There is not enough liquid in the bath  
**Action:** Check for leaks, top up if necessary  
**Action:** Fluid has evaporated, top up if necessary

**AL -P = Pump or motor overloading**

**Cause:** The motor or pump is blocked:  
**Action:** After 10 minutes or longer, the motor temperature should have sunk far enough so that the unit can be switched on again by pressing the reset key. If the circulator switches off again after a short time, return the unit for servicing.

**AL -r = Undefined fault**

**Cause:** This could be caused by a fault which only occurs for a short period of time, i.e. with a fluctuating bath level when the filling level is very close to the minimum.  
**Action:** Top up with heat transfer liquid. The fault is often remedied in this way. In all other cases, the unit must be checked by qualified service personnel.

**AL -F = Sensor breakage or short circuit**

**Action:** The sensor must be exchanged by qualified service personnel. Return unit for repairs.

**B Err = Range exceeded**

**Cause:** The set value and high limit value are cyclically checked for their validity. The fault message “B Err” is shown on the display in case of the range being exceeded. The heating is switched off.  
**Action:** Switch the unit off and start it up again.  
Return the unit for repairs in case of repeated faults.

**S Err = Parity fault**

**Cause:** All data is saved together with a corresponding parity bit in the permanent storage (SRAM). When this data is accessed, the respective parity bit is checked. In case of a parity fault, the fault display “S Err” is shown on the display. The heating then shuts down.  
**Action:** Switch the unit off and start it up again.  
Return the unit for repairs in case of repeated faults.

After the fault is eliminated, the cause of the fault is shown on the display, (e.g. \(^{000}\) F). The preceding three zeros mean that the fault has been eliminated. The reset key must be pressed to start the unit again.
Peristaltic Pumps

The pump-heads of the peristaltic pumps were equipped with lockable guards for increased safety which were locked shut while the pumps were in use. The speed control dial also had a locking knob to prevent accidental speed changes. The tube materials in use with the pumps were compatible with the chemical materials. Silicone tubing (4.8mm) was used with the slurry pumps while Viton tubing (3.2mm) was used to pump the sulphuric acid.

Hotplate

The hotplate was fitted with a warning light to indicate when the top was hot. The light flashed on the front panel when the plate temperature exceeded 60°C and continued even when the heater was turned off as long as the plate temperature was above 60°C and the unit remained connected to the mains electricity supply.

5.4.3 Apparatus Assembly Safety Features

- The entire experimental apparatus was assembled in a containment unit with a drain opening at one end to facilitate any spillages.
- The reaction vessel was constructed from stainless steel 316L to resist the corrosive properties of the reaction mixture.
- The reactor had a wide base to ensure a stationary position in the water bath.
- A stainless steel dip tube was used to disperse sulphuric acid into the reactor.
- The Viton tubing was secured tightly to the stainless steel dip tube and the connected area protected with parafilm. This connection was examined regularly to detect/prevent any leaks.
- The sulphuric acid feed container was covered at all times to prevent exposure to acid fumes. The container was protected from being knocked over by a timber guard at the edge of the work bench.
- The slurry was pumped safely from the feed container by the use of a stainless steel pipe to prevent the silicone tube from being wound onto the agitator shaft.
- The pump tubes were examined regularly for wear and tear.
5.4.4 Materials Safety Data

5.4.4.1 Sulphuric Acid (96% w/w)

Sulphuric acid (96% w/w) was used to decompose calcium citrate to form gypsum. It is a colourless, strongly corrosive, dense, oily liquid. It is miscible with water in all portions. It is not flammable but highly reactive and capable of igniting finely divided combustible materials on contact. It reacts violently with water and organic materials with the evolution of heat. It is extremely hazardous in contact with many materials and it attacks and corrodes many metals by releasing hydrogen.

Contact with the body results in the rapid destruction of tissue, causing severe burns. Repeated contact with dilute solutions can cause a dermatitis, and repeated or prolonged inhalation of a mist of sulphuric acid can cause an inflammation of the upper respiratory tract leading to chronic bronchitis.

Storage containers should be protected against physical damage and contacts with water prevented. It should also be separated from carbides, chlorates, fulminates, nitrates, picrates, powdered metals and combustible materials. Chemical goggles and acid resistant gloves must be worn at all times.

Adequate ventilation should be available in all handling areas. If sulphuric acid comes into contact with the skin or eyes, wash off immediately with large amounts of water and seek medical attention. If the skin contact is extensive, use the safety shower and continue to wash until medical help arrives. If taken internally, sulphuric acid causes severe burns of the mucous of the mouth, throat, stomach, etc. In such an event, dilution of the chemical by drinking large quantities of milk or water may be used until medical help arrives.

Fire involving small amounts of combustibles may be smothered with a suitable dry chemical. Use water on combustibles burning in vicinity of this material but use care as water applied directly to this acid results in evolution of heat and causes splattering. In the event of spills and leakage, cover with sodium carbonate or an equal mixture of soda ash and slaked lime. After mixing, add water if necessary to form a slurry.
5.4.4.2 Citric Acid Solutions
Concentrated citric acid solutions, especially at elevated temperatures are irritants and prolonged skin contact can cause burns. Any contact with the eyes should be flushed with copious quantities of water. Pure citric solutions are not toxic. Care should be exercised in handling of the plant solutions due to the presence of crude impurities, especially sulphuric acid.

5.4.4.3 Gypsum Slurry
Gypsum (or calcium sulphate) is a white, crystalline solid produced in the sour reaction and filtered on the pannevis filter. It is present in the form of filtered cake and aqueous slurry. The filter cake is an inert material, but may contain residual amounts of citric acid. The aqueous slurry contains citric and sulphuric acid impurities and should be handled with care. Contact with the eyes or skin should be avoided. Any contact with the eyes or skin should be flushed with copious quantities of water.

5.4.4.4 Calcium Citrate
Calcium citrate is a white crystalline solid. It is present in the form of aqueous slurry and filtered cake. There are no known health hazards but breathing the dusts should be avoided. Care should also be exercised in handling the slurries due to their elevated temperatures.

5.4.4.5 Acetone
Acetone was used in the laboratory to dry the calcium citrate filter cake for calcium citrate assay determination. It is a colourless, volatile liquid which is freely miscible with water, alcohol, ether, chloroform and oils. It is extremely flammable and is dangerous when exposed to heat, flame or oxidizers. It has a TLV of 1000 ppm and a level of odour perception in air of 1.6ppm. Acetone is narcotic in high concentrations and may cause headache from prolonged inhalation.
All sources of ignition should be eliminated from the storage area and adequate ventilation available. In the event of contact with the body, contaminated skin should be washed with soap and water and the eyes irrigated with water.

In the event of fire, dry chemical, carbon dioxide, alcohol foam or carbon tetrachloride fire extinguishers should be used. Water spray may be ineffective. Spills and leakage can be treated by absorption on paper.

5.4.5 Personal Protection

- Laboratory coats, safety shoes and safety glasses were worn at all times.
- Disposable gloves were used for general laboratory practices such as titrations, calcium citrate assays, microscope slide preparations etc.
- Heavy-duty, heat resistant gloves were used for plant sampling as well as for slurry handling in the laboratory. These gloves were also used when handling hot glassware, sampling from the reactor or removing the reactor from the water-bath.
- Acid resistant gloves were used in all acid handling (setting up and dismantling of the acid feed container, washing of acid tubes and containers).

5.4.6 Waste Disposal

- All waste from the laboratory entered the main plant drainage system leading to the waste water treatment plant.
- Iso-propyl-alcohol was used in the Q.A. laboratory as the solvent for the Malvern particle size analyzer. The waste solvent was stored in a waste container which was removed at regular intervals by Shannon Environmental Services Ltd.
5.5 Hazop Study

A hazard and operability study (HAZOP) is a procedure for the systematic, critical examination of the engineering and operating intentions of a process. When applied to a process design, it indicates potential hazards that may arise from the intended design conditions. For a production plant, a hazard is understood to be an event or sequence of events which may:

- Lead to injury of people, either inside or outside the plant
- Cause environmental damage or insult the environment
- Result in the loss of production quantity, quality or schedule

In the case of this project, a HAZOP was carried out on the experimental reactor in order to identify the potential hazards and resolve them. Since the operation was on a relatively small scale, the main concern was for the safety of the people in the laboratory.

A hazard can only arise if there is a deviation from the expected behaviour. Hypothetical deviations are prompted by using guide words. Guide words are simply words used as keys to suggest the various ways in which deviations from an intention occur. They help generate information and thought about the way deviations from the intended operating conditions can cause hazardous situations. A list and explanation of all the guide words used is given below:

<table>
<thead>
<tr>
<th>Guide word</th>
<th>Deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>No forward flow where there should be.</td>
</tr>
<tr>
<td>More Of</td>
<td>More of any relevant property than there should be</td>
</tr>
<tr>
<td>Less Of</td>
<td>Less of any relevant property than there should be.</td>
</tr>
<tr>
<td>Part Of</td>
<td>Composition of the system may be different than what it should be.</td>
</tr>
<tr>
<td>Reverse</td>
<td>Reverse flow in line.</td>
</tr>
<tr>
<td>As Well As</td>
<td>More components present in the system than there should be.</td>
</tr>
</tbody>
</table>

If the above guide words are applied to the section of the process under scrutiny, a deviation from the normal operation is thus identified and the possible consequences are sought. Once these are identified, corrective action is then recommended. In this Hazop study, only the applicable guide words were used. The lines from the sulphuric acid and the calcium citrate slurry feed supplies to the reactor were examined. The guide words were applied and all meaningful deviations developed. The possible cause and the consequences were examined and the hazards detected and recorded.
<table>
<thead>
<tr>
<th>Guide Word</th>
<th>Deviation</th>
<th>Causes</th>
<th>Consequences</th>
<th>Action</th>
</tr>
</thead>
</table>
| None       | Flow      | 1. No acid supply | No reaction in reactor | A. Ensure adequate acid supply  
|            |           | 2. Failure of acid pump | As for 1 | B. Check supply line for leaks  
|            |           | 3. Blockage of supply line | As for 1  
|            |           |                           | Pressure build-up in line | C. Check that supply line is clear and functional  
| More       | Flow      | 4. Increase in acid pump speed | Increase in acid supply to reactor | D. Isolate acid supply line for maintenance  
|            |           |                           | Increase in reaction exotherm | E. Supply maintenance to pump  
|            | Pressure  | 5. Pump speed too high | Increase in sulphuric acid flowrate  
|            |           |                           | Line rupture | F. Identify, isolate and remove blockage  
|            | Temperature | 6. Line blockage | As for 1 | G. Adjust pump speed setting  
|            |           | 7. Extreme weather conditions | Increased reactant temperature  
|            |           |                           | Dangerous conditions | H. As with G  
|            |           | 8. Fire/explosion in lab. | As for 7 | I. As with F  
| Less       | Flow      | 9. Insufficient sulphuric acid supply | Inadequate conversion of calcium citrate to gypsum  
|            |           |                           | Incomplete reaction | J. Provide sprinkler/fire extinguishing systems  
|            |           | 10. Partial line blockage | As for 9 | K. As with A  
|            |           | 11. Line leaking | As for 9 | L. As with F  
| Reverse    | Flow      | 12. Reverse flow setting on pump active | Back flow towards sulphuric acid feed vessel  
|            |           |                           | No sulphuric acid feed to reactor | M. Isolate area and repair/replace line  
|            |           |                           | No reaction | N. Adjust pump flow direction  
|            |           |                           | Possible contamination of sulphuric acid feed supply with reactor contents |  
| Other      | Maintenance | 13. Equipment failure / leaks | As for None & Less of | O. See actions for None & Less of  

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<thead>
<tr>
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<tr>
<td>A. Ensure adequate slurry supply.</td>
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</tr>
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<td>B. Check supply line for leaks.</td>
<td>B. Check supply line for leaks.</td>
</tr>
<tr>
<td>C. Check that supply line is clear and functional.</td>
<td>C. Check that supply line is clear and functional.</td>
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<tr>
<td>D. Isolate supply line for maintenance.</td>
<td>D. Isolate supply line for maintenance.</td>
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<tr>
<td>E. Supply maintenance to pump.</td>
<td>E. Supply maintenance to pump.</td>
</tr>
<tr>
<td>F. Identify, isolate, and remove blockage.</td>
<td>F. Identify, isolate, and remove blockage.</td>
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<thead>
<tr>
<th>Causes</th>
<th>Consequence</th>
<th>Guide Word</th>
<th>Deviation</th>
<th>Flow</th>
<th>Pressure</th>
<th>Temperature</th>
<th>Less</th>
<th>Reverse</th>
<th>Maintenance</th>
<th>Other</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. No slurry supply</td>
<td>No slurry in reactor for reaction</td>
<td>None</td>
<td>Flow</td>
<td>Flow</td>
<td>Pressure</td>
<td>Temperature</td>
<td>Less</td>
<td>Reverse</td>
<td>Maintenance</td>
<td>Other</td>
</tr>
<tr>
<td>2. Failure of slurry pump</td>
<td>Increase in slurry pump speed</td>
<td>As for 1</td>
<td>Flow</td>
<td>Flow</td>
<td>Pressure</td>
<td>Temperature</td>
<td>Less</td>
<td>Reverse</td>
<td>Maintenance</td>
<td>Other</td>
</tr>
<tr>
<td>3. Blockage of supply line</td>
<td>Increased slurry flowrate to reactor</td>
<td>As for 1</td>
<td>Flow</td>
<td>Flow</td>
<td>Pressure</td>
<td>Temperature</td>
<td>Less</td>
<td>Reverse</td>
<td>Maintenance</td>
<td>Other</td>
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<tr>
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<td>Increased slurry flowrate to reactor</td>
<td>As for 1</td>
<td>Flow</td>
<td>Flow</td>
<td>Pressure</td>
<td>Temperature</td>
<td>Less</td>
<td>Reverse</td>
<td>Maintenance</td>
<td>Other</td>
</tr>
<tr>
<td>5. Pump speed too high</td>
<td>Increased slurry flowrate to reactor</td>
<td>As for 1</td>
<td>Flow</td>
<td>Flow</td>
<td>Pressure</td>
<td>Temperature</td>
<td>Less</td>
<td>Reverse</td>
<td>Maintenance</td>
<td>Other</td>
</tr>
<tr>
<td>6. Line blockage</td>
<td>Line rupture</td>
<td>As for 1</td>
<td>Flow</td>
<td>Flow</td>
<td>Pressure</td>
<td>Temperature</td>
<td>Less</td>
<td>Reverse</td>
<td>Maintenance</td>
<td>Other</td>
</tr>
<tr>
<td>7. Extreme weather conditions</td>
<td>Increased reactant temperature</td>
<td>As for 7</td>
<td>Flow</td>
<td>Flow</td>
<td>Pressure</td>
<td>Temperature</td>
<td>Less</td>
<td>Reverse</td>
<td>Maintenance</td>
<td>Other</td>
</tr>
<tr>
<td>8. Fire/explosion in lab.</td>
<td>Increased reactant temperature</td>
<td>As for 7</td>
<td>Flow</td>
<td>Flow</td>
<td>Pressure</td>
<td>Temperature</td>
<td>Less</td>
<td>Reverse</td>
<td>Maintenance</td>
<td>Other</td>
</tr>
<tr>
<td>9. Insufficient slurry supply conditions</td>
<td>Insufficient product formation</td>
<td>As for 9</td>
<td>Flow</td>
<td>Flow</td>
<td>Pressure</td>
<td>Temperature</td>
<td>Less</td>
<td>Reverse</td>
<td>Maintenance</td>
<td>Other</td>
</tr>
<tr>
<td>10. Partial line blockage</td>
<td>Insufficient product formation</td>
<td>As for 9</td>
<td>Flow</td>
<td>Flow</td>
<td>Pressure</td>
<td>Temperature</td>
<td>Less</td>
<td>Reverse</td>
<td>Maintenance</td>
<td>Other</td>
</tr>
<tr>
<td>11. Line leaking</td>
<td>Backflow towards calcium citrate slurry feed vessel</td>
<td>As for 9</td>
<td>Flow</td>
<td>Flow</td>
<td>Pressure</td>
<td>Temperature</td>
<td>Less</td>
<td>Reverse</td>
<td>Maintenance</td>
<td>Other</td>
</tr>
<tr>
<td>12. Reverse flow setting on pump active</td>
<td>Backflow towards calcium citrate slurry feed vessel</td>
<td>As for 9</td>
<td>Flow</td>
<td>Flow</td>
<td>Pressure</td>
<td>Temperature</td>
<td>Less</td>
<td>Reverse</td>
<td>Maintenance</td>
<td>Other</td>
</tr>
<tr>
<td>13. Equipment failure, leaks.</td>
<td>No slurry feed to reactor</td>
<td>As for 9</td>
<td>Flow</td>
<td>Flow</td>
<td>Pressure</td>
<td>Temperature</td>
<td>Less</td>
<td>Reverse</td>
<td>Maintenance</td>
<td>Other</td>
</tr>
<tr>
<td>14. See actions for</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
5.6 Discussion

The experimental rig was found to be adequate to perform the experimental work described in Chapter 6. Although some problems occurred during the experimental trial period, most of the difficulties were overcome relatively easily and without disruption of the experiment schedule.

After completing the first week of experimental trials, the Orion 720A pH meter was found to be reading incorrectly. Even after calibration of the meter, incorrect readings were obtained for the buffers. A new pH probe was fitted and this gave correct readings for a short term. When this probe created the same problem after a few experiments, it was thought that the probes in use (Orion 8104SC Ross combination pH rugged bulb electrode with screw cap) were not suitable for the application (i.e. continuous operation over a water-bath at 80°C for approximately 2-3 hours). An order was then placed for Sentek PI10-J electrodes which were specially designed to operate at high temperatures. However, these electrodes created the same problem after a few uses. At this stage, the pH meter was thought to be faulty and was returned to the supplier for replacement. A stand-by meter available at ADM was used during the replacement period. The new meter worked well with the normal Ross electrodes and was used successfully for the remainder of the experimental trials.

During some of the trials, the reactor slurry contained significant quantities of grit or other large chunks of solid material. These slurries tended to cause blockages in the tubes of the peristaltic pumps (particularly at the pumpheads) and caused pumping difficulties. To overcome this problem, the flow of slurry through the pump was reversed in order to remove any slurry in the tube. Water was then washed through the tubes.

On selected days, it was difficult to maintain the reactant slurry solids in suspension while the slurry was being heated on the hot-plate prior to addition to reactor. When this problem occurred, the slurry was pumped immediately to the reactor, before the desired temperature was reached. The slurry was then allowed to heat in the reactor prior to the sulphuric acid addition.

The water-bath required two hours heating time before the set-point was reached each day. Since the temperature control unit had to be manually started, a timer switch could not be used. However, although some delays due to the heating period were experienced during the
experimental stage, in most instances, this two hour period was used to sample from the plant and carry out any preliminary laboratory analysis.

The laboratory safety issues addressed in Section 5.4 were very important in establishing an awareness of all the necessary safety features associated with both the equipment and the materials being handled. The Hazop study also ensured an awareness of the hazards associated with the operation of the rig. Overall, a safe working environment was created and maintained as a result of the thorough safety assessment carried out prior to the commencement of work in the laboratory.
Chapter Six

Experimental Work on Laboratory Rig
6.1 Summary

This chapter outlines the experimental work carried out using the laboratory experimental rig described in chapter five. The laboratory experiments were performed with a view to:

- developing an increased technical understanding of the gypsum reaction
- characterising the reaction
- identifying and quantifying the influence of process parameters on the reaction

A series of optimisation experiments were carried out to optimise the laboratory rig set-up and operating conditions. The optimum height of the agitator from the bottom of the reactor was found to be 6cm. The sulphuric acid dip-tube was positioned over the blades of the impeller for the duration of the experimental trials. This position provided adequate sulphuric acid dispersion within the reactor. The optimum agitator speed found was 80% of the maximum. A sulphuric acid flowrate of 47.25 ml/min. was the optimum flowrate. This was achieved by operating at 50% of the maximum pump speed. The optimum reaction temperature was found to be 80°C. Once the optimum set-up and operating conditions were determined, a trial verified that the plant results were reproducible at these conditions. These conditions were held constant for the duration of the trial work.

The results obtained from the intensive experimentation period described in this chapter are summarised as follows:

During the database development (Section 3.3.3), it was thought that the pump transferring the calcium citrate slurry to the filters was causing crystal damage. Laboratory experiments verified that the transfer pump was not the cause of the significant decrease in mean particle size between the calcium citrate slurry and filter cake samples. The particle size decrease is actually caused by the presence of large grit particles in the slurry which settle out before reaching the filters and as a result, are not present in the cake samples.

It was found that even when the calcium citrate conversion was complete, the addition of sulphuric acid increased the mean particle size. This increase in mean particle size was proved to be a result of the additional acid being added and not due to residence time in the reactor.
Residence time alone was not found to influence the gypsum crystal size. Therefore, extending the gypsum slurry capacity in the plant to increase the residence time of the crystals would not appear to be of benefit to the gypsum crystal size.

A slight improvement in mean particle size and filterability results was observed when the reaction was performed using lower concentrations of sulphuric acid. However, these improvements were not significant enough to warrant further investigation.

Microcrystalline hemihydrate material was successfully formed by using high \( \text{H}_2\text{SO}_4 \) flowrates and low agitation speeds to create 'hot-spots' within the reactor. The filtration of the slurry proved that the material was capable of getting through the filter cloth which, in the plant scale, would then be undesirably present in the refining end. A high possibility of filter cloth blinding also existed which would be detrimental to the gypsum filtration step. These trials demonstrated the conditions which should be avoided in the plant at all times in an effort to eliminate the production of hemihydrate gypsum. The resulting effects of the undesirable conditions were also clearly illustrated.

The absence of fine particles from the gypsum slurry had no significant effect on the particle size distribution. This suggested that the fine particles of hemihydrate gypsum in the presence of a dihydrate gypsum sample are not significant enough to be recognised by the Malvern instrument. However, as illustrated in Section 6.5.4, significant quantities of hemihydrate gypsum were recognisable by the Malvern.

The reaction of \( \text{H}_2\text{SO}_4 \) with calcium citrate cake, produced low quality crystals with poor washing and filtration characteristics. The physical nature of the slurry also suggested handling difficulties which, in the large scale would pose a problem. This trial emphasised the necessity of the reaction to take place in a slurry form, with the \( \text{H}_2\text{SO}_4 \) added below the slurry surface.

Trials with calcium citrate slurry suggested significant improvements in the gypsum crystals and hence improved filtration rates. Plate-like parallelogram-shaped crystals of gypsum were formed and the filterability result appeared to be much improved on the control samples. This reaction of calcium citrate to gypsum in the presence of the citric acid mother liquor, gave
promising initial results with a view to the development of a possible solution to the plant gypsum filtration problems.

The presence in the reaction, of citric acid mother liquor from the pannevis filtrate, did not have the same improved effect on the gypsum crystals as the calcium citrate slurry reaction. This suggested that some impurity present in the citric acid liquor prior to the calcium citrate filtration stage (but not present in the liquor remaining after the pannevis filtration), had a positive effect on the crystals.

Reactions using water to slurry the calcium citrate cake produced small, needle-shaped crystals.

Microscopic analysis of the initial trials using filtrate from the calcium citrate filtration step to slurry the calcium citrate cake, clearly illustrated that much better crystals were achieved. This result agreed with those obtained using calcium citrate slurry. The Malvern analysis also supported the microscopic evidence of improved crystal size with mean particle sizes of approximately double the control values achieved. These trials, combined with the trial using filtrate from the pannevis filtration step, enhanced the previous suggestion that some impurity removed at the calcium citrate filtration stage, had a beneficial effect on the gypsum crystals.

Continuing trials rejected this theory while suggesting that the improved crystals obtained previously were as a result of a much lower slurry specific gravity. The experiments performed with slurries of high specific gravity showed no improvement in crystal size or appearance.

Preliminary experiments in the presence of Sodium and Potassium Citrate impurities suggested a positive influence on the gypsum crystals. Although the Malvern results were found to be relatively normal with the Potassium Citrate alone, when analysed microscopically, the crystals appeared much better than the usual gypsum crystals. Larger Malvern results were achieved in the presence of Sodium Citrate. This was explained by longer longitudinal axes of the crystals when analysed microscopically. The volume of particles in the tail of the distribution appeared smaller in the experiment with Sodium Citrate alone (only 10% of particles smaller than 26μm). This theory of crystal improvements as a result of Sodium and Potassium Citrate impurities was eliminated however by further experimentation. It was found that with a high
dilution factor, improvements in crystal size and overall crystal appearance could be obtained, with or without the Sodium or Potassium Citrate.

Since the citric acid broth from the fermentation stage of the process contains both soluble and insoluble impurities, in order to determine the influence (if any) of these impurities on the gypsum formation step, additional quantities of the cationic impurities were added to the reaction mixture.

The addition of $\text{K}_2\text{SO}_4$ did not influence the gypsum crystals. The mean particle sizes remained practically unchanged and any fluctuations in the filtration rates were not significant. Since the potassium remained in the citric acid solution after the conversion to gypsum had taken place, increase of the impurity concentration above the concentrations tested, did not seem practical.

The addition of $\text{Na}_2\text{SO}_4.10\text{H}_2\text{O}$ to the reaction system appeared to have a marginal negative effect on the gypsum produced. A slight decrease in the mean particle size was evident and a deterioration in the filtration rate was also experienced in the presence of the impurity.

The laboratory experiments with high impurity contents of $\text{MgSO}_4.7\text{H}_2\text{O}$ showed very significant changes in the particle size distributions but the slurry filtration rates did not change. Initial speculation suggested that although the overall particle distribution improved considerably, the filterability was inhibited by the presence of such large quantities of impurity. However, the fact that the particle size distribution improved once the impurity was added (even prior to the reaction) suggested that some of the impurity did not dissolve completely and the increase in particle size was actually due to particles of the impurity in the sample. The fact that no visible change in crystal size was evident from the microscopic analysis also supported this theory.

The addition of $\text{FeSO}_4.7\text{H}_2\text{O}$ to the reaction system produced results similar to those obtained from the addition of $\text{MgSO}_4.7\text{H}_2\text{O}$. Considerable changes in the particle size distributions were obtained while the slurry filtration rates were not altered. However, crystals of $\text{FeSO}_4$ were identified in these experiments which verified that the change in the particle size distributions was due to crystals of the impurities as opposed to changes in the actual gypsum crystals.
In practical terms, the quantities of impurities used for these experiments were unrealistic for the plant operation. Atomic Absorption analysis also proved that a significant quantity of the impurity remained in solution after filtration, therefore, on the plant scale, the impurities would be undesirably present in the citric acid solution. However, it was hoped that if the gypsum crystal habit was altered by such an impurity, research into the identification of a substance similar in its habit modifying properties to the impurities tested, but effective in minute quantities could then be addressed.

Although Fe$_2$(SO$_4$)$_3$.xH$_2$O and Al$_2$(SO$_4$)$_3$.16H$_2$O impurities had a positive influence on the gypsum produced in the phosphoric acid process (Hasson et al, 1990), they were not found to have the same effect on the gypsum produced in the citric acid process.

The gypsum obtained from pure reactants appeared to be of better quality than the crystals normally formed. [The calcium citrate formed from the plant reactants appeared to be less uniform in shape to that obtained from the pure reactants]. The mean particle size of the calcium citrate cake obtained after filtration and washing, was close to that obtained from the pure reactants as well as from the plant calcium citrate. The filtration rates of the gypsum slurries could not be compared to the plant rates due to their lower specific gravities (resulting from the reaction with calcium citrate slurry, as opposed to the normal decomposition of calcium citrate cake slurried with gypsum slurry recycle from the strike tank).

On completion of the intensive experimentation performed in this study, it appears that it is not possible to improve the gypsum crystal size and filtration rate while the vortex mixer is on-line. Experiments carried out on the gypsum slurry (after the vortex mixer) demonstrated that once the crystals have been formed, the crystal size cannot be increased by any chemical means. At this stage, the crystals have been fragmented and therefore their filtration rate has been decreased. The reactions carried out using calcium citrate and sulphuric acid proved that the most significant improvement in gypsum crystal size was obtained when the reaction was performed at a low specific gravity. The addition of impurities to act as habit modifiers did not succeed to influence the crystals as found by researchers in the phosphoric acid industry.
6.2 Introduction

Intensive laboratory investigations were carried out on the experimental rig with a view to:

- Developing a detailed technical understanding of the factors which influence the nucleation of gypsum crystals and the resultant filterability of gypsum.
- Characterising the reaction between calcium citrate and sulphuric acid (96% w/w).
- Quantifying the influence of process parameters on the gypsum production reaction.

The investigations are discussed under the following categories:

- Optimisation experiments
- Step-wise sulphuric acid addition
- Variation in sulphuric acid concentration
- Residence time investigation
- Formation of hemihydrate gypsum
- Reaction of $\text{H}_2\text{SO}_4$ (96% w/w) with calcium citrate cake
- Reaction of $\text{H}_2\text{SO}_4$ (96% w/w) with calcium citrate slurry (without plant recycle)
- Reaction of $\text{H}_2\text{SO}_4$ (96% w/w) with calcium citrate cake slurried in pannevis filtrate
- Reaction of $\text{H}_2\text{SO}_4$ (96% w/w) with calcium citrate cake slurried in water
- Impurity investigations
- Reaction of $\text{H}_2\text{SO}_4$ (96% w/w) with pure calcium citrate formed from pure reagents

The objectives and procedure of each investigation are outlined, followed by details of the results. Each set of results is analysed and discussed and the conclusions given.
6.3 Experimental Trial Procedure

The same basic experimental procedure was used in all the trials to ensure result consistency. After verifying that the plant results could be achieved in the laboratory (see Section 6.4.5), the plants trim tank was used as the control for each trial. The reaction controlling mechanism used was pH. The general experimental trial procedure is described below.

Plant production data was recorded from the control room. The temperature of the water bath was set at 80°C and allowed to reach the set-point. Calcium citrate slurry was collected from the plant sample point. A sample was taken from the trim tank and the slurry temperature recorded. The calcium citrate slurry was maintained at approximately 70-75°C on a hot-plate and stirred continuously until the water bath set-point was reached. The pH of the trim tank sample was measured to obtain the target pH for the laboratory reaction. A filterability test was performed on the trim tank sample and the filtrate retained. Calcium citrate slurry (4.35 litres) was pumped to the reactor. The reactor agitator motor was switched on. The pH and temperature probes were placed in the reactor and the pH and temperature readings were allowed to stabilize. The \( \text{H}_2\text{SO}_4 \) pump speed was set to give the desired acid flowrate and \( \text{H}_2\text{SO}_4 \) was pumped to the reactor via the dip-tube until the target pH was reached. Temperature and pH readings were taken at regular intervals during the reaction. When the pH had stabilized at the target value, a sample was taken. A filterability test was performed on the laboratory sample and the filtrate was retained. All filterability tests were carried out at the same temperature. Calcium citrate assays were done to determine the quantity of calcium citrate (if any) present in the samples. This gave a measure of the degree of calcium citrate conversion to gypsum. All samples were analysed using the Malvern Mastersizer to determine the crystal size distributions. Photograph records were taken of the microscopic analysis. Solids tests were performed on the filtrates. The filtrates were analysed using Atomic Absorption for the impurity investigations.

Depending on the particular experiment being performed, this procedure varied slightly from trial to trial. The variation was mainly due to the number of samples taken, the sample times, or the analysis application. Some of the analysis was not applicable for selected trials and may therefore have been eliminated from the procedure.
6.4 Optimisation of Laboratory Experimental Rig

6.4.1 Introduction

Prior to any investigation trials, the optimum set-up and conditions for the laboratory apparatus were determined. The height of the agitator from the bottom of the reactor and the position of the acid dip-tube were varied to determine the optimum set-up. The agitator speed, sulphuric acid flowrate and the reaction temperature were the operating conditions to be optimised. Once the optimum set-up and operating conditions were determined, a trial was carried out to verify that the plant results were reproducible at the optimum settings (see Section 6.4.5). The optimum conditions were then held constant for the duration of the trial work. (Note, during selected trials, these conditions had to be varied for specific reasons. These exceptions are explained in the individual experiment descriptions).

6.4.2 Optimisation Sequence

The following procedure sequence was used to optimise the laboratory rig.

- The flowrate of acid to the reactor was set at a constant value and the same volume of calcium citrate slurry from the plant sample point used for each trial.
- The height of the agitator shaft from the top of the reactor to the middle of the blade area was measured. This height was held constant.
- The height of the acid dip tube from the top of the reactor to the discharge points of the tube was measured and this height was held constant.
- The temperature of the water bath was set at a constant temperature of 80°C.
- The degree of agitation in the reactor was varied while using the same acid flowrate and sample times. The procedure was repeated for a variety of agitator speeds.
- When the optimum agitator speed was decided, the position of the dip tube was varied, again using the same acid flowrate and sample times. Trials were carried out with the acid discharging from the dip tube positioned both under and over the agitator blades. The optimum dip tube position was found.
- The flowrate of acid to the reactor was increased, but still just enough acid was added to reach the target pH. The optimum acid flowrate was found.
- The temperature of the water-bath was changed while using the optimum conditions found as described above. The optimum reaction temperature was determined.
6.4.3 Description of Optimisation Experiments

EXPERIMENT 1: Determination of Optimum Agitator Speed

Objective:
Determine the optimum agitator motor speed by carrying out a series of experiments with the speed setting at various percentages of the maximum.

Reaction Conditions:
- Agitator Motor Speed: Variable
- Reaction Temperature: 80°C
- H₂SO₄ Concentration: 96% w/w
- H₂SO₄ Flowrate: 22.4 ml/min.

Procedure:
The agitator speed was set at 80% of the maximum for Trial 1.1. The temperature and pH values were recorded during the acid addition. The H₂SO₄ was added to give a pH of approximately 0.85. A sample was taken at 20 minutes and the reaction mixture was then left to stir in the reactor until a further sample was taken at 73 minutes. The entire apparatus was fully cleaned and the procedure repeated with the agitator speed at 100% (Trial 1.2). Agitation in the reactor appeared difficult with the agitator motor speed set at less than 80% of the maximum, hence the minimum speed investigated was 80%. A comparison was made between the results of both trials.

Results:
The filterability test, calcium citrate assay and particle size results are given in Table 6.1 and an overlay plot of the Malvern particle size distributions can be seen in Appendix E.

<table>
<thead>
<tr>
<th>Filterability Test (ml/min.)</th>
<th>Test Temp. (°C)</th>
<th>Calcium Citrate Assay (% Calcium Citrate)</th>
<th>M.P.S. (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control Sample</td>
<td>1000</td>
<td>47</td>
<td>0.86</td>
</tr>
<tr>
<td>Trial 1.1 Sample</td>
<td>1125</td>
<td>47</td>
<td>0.48</td>
</tr>
<tr>
<td>Trial 1.2 Sample</td>
<td>900</td>
<td>45</td>
<td>0.98</td>
</tr>
</tbody>
</table>

Table 6.1: Results from Trials 1.1 and 1.2

The temperature and pH values recorded during the trials are given in Table 6.2.
### Table 6.2: Temperature and pH Recordings during Trials 1.1 & 1.2

<table>
<thead>
<tr>
<th>Time (minutes)</th>
<th>Trial 1.1 Temp. (°C)</th>
<th>Trial 1.2 Temp. (°C)</th>
<th>Trial 1.1 pH</th>
<th>Trial 1.2 pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>76.4</td>
<td>76.4</td>
<td>1.465</td>
<td>1.383</td>
</tr>
<tr>
<td>1.0</td>
<td>76.5</td>
<td>76.5</td>
<td>1.463</td>
<td>1.382</td>
</tr>
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<td>1.5</td>
<td>76.8</td>
<td>76.9</td>
<td>1.433</td>
<td>1.360</td>
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<td>1.351</td>
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<td>78.3</td>
<td>1.415</td>
<td>1.340</td>
</tr>
<tr>
<td>3.0</td>
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<td>78.9</td>
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<td>0.773</td>
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<td>78.3</td>
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<td>77.4</td>
<td>0.769</td>
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<td>76.5</td>
<td>0.702</td>
<td>0.713</td>
</tr>
</tbody>
</table>

Analysis and Discussion of Results:

The temperature and pH values from both trials were plotted against time. The resulting plots are shown in Figure 6.1. From Figure 6.1, it appears that the temperature trend did not vary between the two trials. The starting temperatures were identical in both cases, the temperature increased rapidly, as expected, during the acid addition stage and then decreased gradually with time when the acid addition was complete. The pH trend illustrated a difference in starting pH
values for both trials. Since the same initial slurry was used for both trials, this difference in pH was explained by slightly inconsistent pH meter readings (see Section 5.6). The pH trends were seen to merge once the sulphuric acid addition was complete, and both trials illustrated the expected pH levelling off as equilibrium was reached in the reactor.

The filterability result from trial 1.1 was better than trial 1.2. However, a difference of 2°C in the test temperatures was likely to influence the result. The calcium citrate assay results illustrated that the conversion to gypsum was complete at sample time (see Section 4.8). The slight variations between results was most likely to be related to the analytical technique. Comparison of the Malvern mean particle sizes shows a slight deviation between results with a slightly smaller mean particle size achieved when the higher agitator speed was used.

Conclusions:
The results for the lower agitator speed (trial 1.1) were found to be marginally better than the maximum speed, although observation during the trials suggested that equilibrium in the reactor was achieved slightly quicker with the higher agitation. In conclusion, it was decided to use the 80% speed as the optimum agitator speed. However, the solids content of the plant slurry varied slightly from day to day, depending on the recycle rate of gypsum slurry to the calcium citrate filter repulper. Therefore, if the solids content was higher on a particular day, a higher agitation speed was necessary for adequate agitation. As proved, the results were not altered significantly by a change from 80% to max. speed so this increase in agitator speed was not seen as an influencing factor.
EXPERIMENT 2: Determination of Optimum H₂SO₄ Dip-Tube Position

Objective:

Determine the optimum sulphuric acid dip-tube position by securing the dip-tube in different positions in the reactor for two similar experiments.

Reaction Conditions:

- Agitator Motor Speed: 100%
- Reaction Temperature: 80°C
- H₂SO₄ Concentration: 96% w/w
- H₂SO₄ Flowrate: 22.4 ml/min.

Procedure:

The sulphuric acid dip-tube was secured above the agitator for the first trial and below the agitator for the second trial. H₂SO₄ was added to the slurry in the reactor to give a pH of approx. 0.9 in both trials (actual pH = 0.836 and 0.821 respectively at sample times). Each experiment was run for 20 minutes before sampling. The reactor mixture was also observed during the trial so that any changes in the texture of the mixture as a result of the difference in sulphuric acid entry point could be detected.

Results:

The filterability test, calcium citrate assay and particle size results are given in Table 6.3 and an overlay plot of the Malvern particle size distributions can be seen in Appendix E.

<table>
<thead>
<tr>
<th>Filterability Test (ml/min.)</th>
<th>Test Temp. (°C)</th>
<th>Calcium Citrate Assay (% Calcium Citrate)</th>
<th>M.P.S. (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control Sample</td>
<td>---</td>
<td>---</td>
<td>46.55</td>
</tr>
<tr>
<td>Trial 2.1 Sample</td>
<td>1000</td>
<td>0.24</td>
<td>42.32</td>
</tr>
<tr>
<td>Trial 2.2 Sample</td>
<td>1000</td>
<td>0.98</td>
<td>42.84</td>
</tr>
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</table>

Table 6.3: Results from Trials 2.1 and 2.2

The temperature and pH values recorded during the trials are given in Table 6.4.
Table 6.4: Temperature and pH Recordings during Trials 2.1 and 2.2

<table>
<thead>
<tr>
<th>Time (minutes)</th>
<th>Trial 2.1 Temp. (°C)</th>
<th>Trial 2.2 Temp. (°C)</th>
<th>Trial 2.1 pH</th>
<th>Trial 2.2 pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>76.2</td>
<td>76.2</td>
<td>1.527</td>
<td>1.517</td>
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<tr>
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<td>0.823</td>
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<td>77.0</td>
<td>0.838</td>
<td>0.823</td>
</tr>
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<td>77.0</td>
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<td>76.9</td>
<td>0.836</td>
<td>0.821</td>
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</table>

Analysis and Discussion of Results:

The temperature and pH values from both trials were plotted against time. The resulting plots are shown in Figure 6.2. From Figure 6.2, it appears that the temperature trend varied slightly between the two trials. Although the starting temperatures were identical in both cases, the temperature seemed to increase more rapidly for Trial 2.2 and the peak temperature was
reached earlier than in Trial 2.1. This was because the acid dip-tube was not emptied before the second experiment. Therefore, the acid reached the reactor almost immediately as no time was required to fill the acid tube. For the same reason, the drop in pH was also seen to occur sooner than for Trial 2.1. Both trials again illustrated the expected pH levelling off as equilibrium was achieved in the reactor.

![Figure 6.2: Plots of Temperature and pH versus Time for Trials 2.1 & 2.2](image)

The filterability results suggested no difference between the trials. The slight variation between results of the calcium citrate assays was most likely to be related to the analytical technique. Comparison of the Malvern mean particle sizes showed no difference between the samples from both trials, although the sizes did unexpectedly deviate from the control sample. For the purposes of these trials however, this result was not important.

**Conclusions:**

Overall, it seems that the position of the sulphuric acid dip-tube did not influence the results. From Sohnel and Garside, 1992, when precipitation is carried out by adding a solution of one reactant to a second reactant solution already present in a vessel, the feed point location may only be important if the stirring is inadequate. For well-stirred systems, the influence is generally negligible. The reaction system in this case is well-stirred, therefore, the dip-tube position is not an influencing factor, as proved experimentally. The dip-tube was positioned above the agitator for the continuing experimental trials.
EXPERIMENT 3: Determination of Optimum Sulphuric Acid Flowrate

**Objective:**

Determine the optimum sulphuric acid flowrate for the gypsum reaction.

**Reaction Conditions:**

- Agitator Motor Speed: 80% of Max.
- Reaction Temperature: 80°C
- H$_2$SO$_4$ Concentration: 96% w/w
- H$_2$SO$_4$ Flowrate: Variable

**Procedure:**

For the initial optimisation experiments, the H$_2$SO$_4$ pump speed was set at 25% of the maximum. From the pump calibration curve, (see Appendix D), this speed corresponded to a flowrate of 22.4 ml/min. This low flowrate enabled the H$_2$SO$_4$ addition to be easily controlled. However, when the entire trial procedure became very familiar, it was possible to control the H$_2$SO$_4$ addition at a higher flowrate. Therefore, the H$_2$SO$_4$ pump speed was adjusted to 50% of the maximum which gave a flowrate of 47.25 ml/min. This enabled the trials to be carried out in less time which facilitated the completion of more than one trial per day. Pump speeds above 50% of the maximum were also tried but the control of H$_2$SO$_4$ addition became difficult at these higher flowrates.

**Conclusion:**

The optimum H$_2$SO$_4$ flowrate was found to be 47.25 ml/min. This was achieved by operating at 50% of the maximum pump speed.

EXPERIMENT 4: Determination of Optimum Reaction Temperature

**Objective:**

Determine the optimum reaction temperature by carrying out a series of trials with the water-bath temperature set at different values (i.e. 20, 30, 40, 50, 60, 80 and 90°C)
Reaction Conditions:
- Agitator Motor Speed: 100% for 20-60°C trials, 80% for 80, 90°C trials
- Reaction Temperature: Variable
- \( \text{H}_2\text{SO}_4 \) Flowrate: 47.25 ml/min.
- \( \text{H}_2\text{SO}_4 \) Concentration: 96% w/w

Procedure:
Experiments were carried out at 20, 30, 40, 50, 60, 80 and 90°C. Two experiments were carried out on a particular day, but due to the variation in slurry from day to day, it was difficult to compare the results of the range of temperature settings with each other. Using the strike and trim tanks as control samples however, results from each temperature trial was compared to the normal temperature setting (80°C). Agitation was difficult at the low temperature settings due to the more viscous nature of the slurry and therefore it was not practical to run at very low temperatures. It was not feasible to operate the water bath in the laboratory at higher than 90°C.

Results:
The mean particle size results from the temperature trials are given in Table 6.5. The target and actual pH measurements are also shown to illustrate the success of the pH control mechanism for the reaction.

<table>
<thead>
<tr>
<th>Bath Temp. (°C)</th>
<th>Plant Trim MPS (μm)</th>
<th>Lab. Trim MPS (μm)</th>
<th>Target pH</th>
<th>Actual pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>57.35</td>
<td>53.49</td>
<td>1.099</td>
<td>1.010</td>
</tr>
<tr>
<td>30</td>
<td>45.49</td>
<td>45.06</td>
<td>0.878</td>
<td>0.874</td>
</tr>
<tr>
<td>40</td>
<td>45.49</td>
<td>43.97</td>
<td>0.890</td>
<td>0.891</td>
</tr>
<tr>
<td>50</td>
<td>54.89</td>
<td>51.37</td>
<td>0.552</td>
<td>0.560</td>
</tr>
<tr>
<td>60</td>
<td>54.89</td>
<td>52.55</td>
<td>0.599</td>
<td>0.599</td>
</tr>
<tr>
<td>80</td>
<td>45.16</td>
<td>45.31</td>
<td>0.635</td>
<td>0.643</td>
</tr>
<tr>
<td>90</td>
<td>49.46</td>
<td>49.60</td>
<td>0.652</td>
<td>0.639</td>
</tr>
</tbody>
</table>

Table 6.5: Temperature Trial Results

Analysis and Discussion of Results:
A bar chart illustrating the difference between the plant and laboratory samples mean particle sizes is shown in Figure 6.3.
From Figure 6.3, it is evident that the plant results were reproduced at the 80 and 90°C trials. At the lower temperatures, the mean particle size results obtained were lower than the corresponding plant results. The filterability results were also found to be very poor at the low temperatures (as expected, see Section 4.5) and agitation in the reactor was also difficult. The calcium citrate assay results were used to verify the conversion of calcium citrate to gypsum. The target and actual pH values given in Table 6.5 illustrated the suitability of the pH control mechanism for the experiments.

Conclusions:

The plant results were achieved at temperatures of 80 and 90°C while the mean particle sizes obtained were smaller than the plant results at the lower temperatures. The optimum temperature was therefore taken to be 80°C. The reproducible results at this temperature also verified the success of pH control for the gypsum reaction.

6.4.4 Summary of Optimisation Experiments

The optimum agitator speed was found to be 80% of the maximum. The dip-tube was positioned above the agitator for the optimum set-up. A sulphuric acid flowrate of 47.25 ml/min. was found to be the optimum. The optimum temperature was found to be 80°C.
6.4.5 Verification of Plant Reproducibility

Objective:
Verify that the laboratory apparatus can reproduce the plant results by using the optimum conditions summarised in Section 6.4.4.

Procedure:
Calcium citrate slurry was collected from the plant sample point. A sample was taken from both the strike and trim tanks and the pH of each sample was measured (strike pH = 1.261, trim pH = 0.861). These pH values were used as the target pH values during the reaction. The sulphuric acid was added to the reactor until the target strike pH was reached. A sample was taken at this stage. More sulphuric acid was then added to obtain the target trim pH and another sample was taken. Calcium citrate assays and Malvern particle size measurements were performed on both the plant and laboratory samples.

Results:
The results of this trial are given in Table 6.6 below.

<table>
<thead>
<tr>
<th></th>
<th>pH</th>
<th>MPS (µm)</th>
<th>% Calcium Cit.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plant Strike Sample</td>
<td>1.261</td>
<td>42.45</td>
<td>0.613</td>
</tr>
<tr>
<td>Lab. Strike Sample</td>
<td>1.207</td>
<td>41.31</td>
<td>0.536</td>
</tr>
<tr>
<td>Plant Trim Sample</td>
<td>0.861</td>
<td>45.16</td>
<td>0.362</td>
</tr>
<tr>
<td>Lab. Trim Sample</td>
<td>0.871</td>
<td>45.31</td>
<td>0.369</td>
</tr>
</tbody>
</table>

Table 6.6: Results from Verification Trial

Analysis and Discussion of Results:
The results given in Table 6.6 above, illustrate that the variation in mean particle size results between the plant and laboratory samples was minimal. The calcium citrate assay results also indicate little difference between the plant and laboratory samples.

Conclusion:
This trial successfully verified that the plant results could be reproduced using the laboratory apparatus. Therefore, it was acceptable to use the plants trim tank sample as the control sample for the experimental investigations described in Section 6.5.
6.5 Experimental Investigations

Once the optimum set-up and conditions were found, the actual investigating trials began. In each case, the trial procedure was repeated as often as necessary to verify any conclusions. Each investigation is discussed in detail in the following sections.

6.5.1 Investigation 1: Step-Wise Addition of $\text{H}_2\text{SO}_4$

Objective:
Investigate the stages of the gypsum formation reaction by examining the influence of $\text{H}_2\text{SO}_4$ addition to the calcium citrate slurry.

Procedure:
The $\text{H}_2\text{SO}_4$ was added to the reactor in a step-wise manner. After each 1 minute or 30 second addition of acid, the reaction mixture was allowed to equilibrate in the reactor for 10 minutes. Samples were taken at the end of each equilibration period. A one hour residence time period was included during trial number 1.3, after which further quantities of acid were added. Calcium citrate assays on the samples established the degree of calcium citrate conversion to gypsum at the various reaction stages.

Results:
The results from the trials are given in Tables 6.7 and 6.8.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>TRIAL NO. 1.1</th>
<th>TRIAL NO. 1.2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Vol. $\text{H}_2\text{SO}_4$ (mls)</td>
<td>% Calcium Citrate</td>
</tr>
<tr>
<td>1</td>
<td>0.0</td>
<td>---</td>
</tr>
<tr>
<td>2</td>
<td>22.4</td>
<td>36.51</td>
</tr>
<tr>
<td>3</td>
<td>44.8</td>
<td>---</td>
</tr>
<tr>
<td>4</td>
<td>67.2</td>
<td>---</td>
</tr>
<tr>
<td>5</td>
<td>89.6</td>
<td>---</td>
</tr>
<tr>
<td>6</td>
<td>112.0</td>
<td>0.853</td>
</tr>
<tr>
<td>7</td>
<td>134.4</td>
<td>0.491</td>
</tr>
<tr>
<td>8</td>
<td>134.4</td>
<td>0.493</td>
</tr>
<tr>
<td>9</td>
<td>134.4</td>
<td>---</td>
</tr>
</tbody>
</table>

Table 6.7: Results from Trial Nos. 1.1 and 1.2
Chapter Six - Laboratory Investigations

<table>
<thead>
<tr>
<th>TRIAL NO. 1.3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample No.</td>
</tr>
<tr>
<td>1</td>
</tr>
<tr>
<td>2</td>
</tr>
<tr>
<td>3</td>
</tr>
<tr>
<td>4</td>
</tr>
<tr>
<td>5</td>
</tr>
<tr>
<td>6</td>
</tr>
<tr>
<td>7</td>
</tr>
<tr>
<td>8</td>
</tr>
<tr>
<td>9</td>
</tr>
<tr>
<td>10</td>
</tr>
<tr>
<td>11</td>
</tr>
<tr>
<td>12</td>
</tr>
</tbody>
</table>

Table 6.8: Results from Trial No. 1.3

Analysis and Discussion of Results:

The temperature and pH trends recorded during the trials are illustrated graphically in Figures 6.4 (a), (b) and (c) from which the stages of the H₂SO₄ addition are clearly evident.

Figure 6.4(a): Temperature and pH Trends - Trial No. 1.1

Figure 6.4(b): Temperature and pH Trends - Trial No. 1.2
Figures 6.5(a), (b) and (c) illustrate the relationship found between the quantity of acid added and the mean particle size of gypsum formed. Figures 6.5(b)/(c) include the % calcium citrate to illustrate the degree of calcium citrate conversion in relation to the other parameters.

It is evident that the mean particle size gradually increased with the acid volume added, even after the calcium citrate conversion was complete. The mean particle size did not change during the 1 hour residence time period in trial number 1.3 and when acid was added after the hour, the mean particle size began to increase again.
Conclusions:
It was found that even when the calcium citrate conversion was complete, the addition of sulphuric acid increased the mean particle size. It was also concluded that the continual increase in mean particle size after the calcium citrate was fully converted, was a result of the additional acid being added and not due to residence time in the reactor.

6.5.2 Investigation 2: Influence of Residence Time

Objective:
Determine the influence of residence time on the gypsum crystals.

Procedure:
This investigation was carried out in conjunction with many of the other investigating trials. After the target pH was reached in a particular trial, a sample was taken. The reaction mixture was allowed to agitate in the reactor for various periods of residence time, after which additional samples were taken.

Results:
Table 6.9 shows the Malvern results from sets of two samples taken with residence time periods of 1 hour, 1 hour, 0.75 hour and 1.5 hours respectively between them. These samples were taken from selected trials during the laboratory investigations.

<table>
<thead>
<tr>
<th>Set No.</th>
<th>Sample 1 D(v,0.5)</th>
<th>Sample 2 D(v,0.5)</th>
<th>Sample 1 D(v,0.1)</th>
<th>Sample 2 D(v,0.1)</th>
<th>Sample 1 D(v,0.9)</th>
<th>Sample 2 D(v,0.9)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>50.51</td>
<td>51.29</td>
<td>12.90</td>
<td>12.92</td>
<td>107.52</td>
<td>106.82</td>
</tr>
<tr>
<td>2</td>
<td>49.60</td>
<td>49.32</td>
<td>13.56</td>
<td>13.27</td>
<td>103.17</td>
<td>102.45</td>
</tr>
<tr>
<td>3</td>
<td>44.77</td>
<td>45.30</td>
<td>10.24</td>
<td>10.39</td>
<td>119.43</td>
<td>118.92</td>
</tr>
<tr>
<td>4</td>
<td>55.59</td>
<td>56.20</td>
<td>13.65</td>
<td>13.92</td>
<td>110.27</td>
<td>110.16</td>
</tr>
</tbody>
</table>

Table 6.9: Residence Time Investigation Results

Analysis and Discussion of Results:
Table 6.9 shows the mean particle size results along with the 10% and 90% cut-off points. These percentile points were examined to determine any changes, not only in the mean particle
size, but also in the upper and lower ends of the distribution. If any breakage or attrition of crystals was occurring due to the agitation in the reactor during the residence time period, changes in the upper and lower ends of the distribution would be evident. From the results given in Table 6.9 along with the graphical analysis shown in Figure 6.6, very little change was apparent between the samples taken before and after the residence time period.

![Graphical Analysis - Residence Time Investigations](image)

**Figure 6.6: Graphical Analysis - Residence Time Investigations**

The slight fluctuations in results cannot be taken as significant, given that any one sample analysed repeatedly with the Malvern, is capable of giving variations of ~1-2\( \mu \)m between results (see Section 4.3.5).

**Conclusion:**

Residence time alone was not found to influence the gypsum crystal size. Therefore, extending the gypsum slurry capacity in the plant to increase the residence time of the crystals would not be of benefit to the gypsum crystal size.
6.5.3 Investigation 3: Variation in $\text{H}_2\text{SO}_4$ Concentration

**Objective:**

Investigate the effects of using a lower sulphuric acid concentration (i.e. 50% v/v $\text{H}_2\text{SO}_4$ versus 96% w/w $\text{H}_2\text{SO}_4$)

**Procedure:**

Trials were carried out with 50% v/v $\text{H}_2\text{SO}_4$ as opposed to the usual 96% w/w $\text{H}_2\text{SO}_4$ and the normal experimental procedure was then followed (see Section 6.2).

**Analysis and Discussion of Results:**

The results from the trials are given in Tables 6.10(a), (b) and (c).

<table>
<thead>
<tr>
<th></th>
<th>Filterability Test (ml/min.)</th>
<th>Test Temp. ($^\circ$C)</th>
<th>Calcium Citrate Assay (% Calcium Citrate)</th>
<th>M.P.S. (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control Sample</td>
<td>---</td>
<td>---</td>
<td>0.494</td>
<td>32.06</td>
</tr>
<tr>
<td>Sample 1</td>
<td>794</td>
<td>58</td>
<td>0.469</td>
<td>33.74</td>
</tr>
<tr>
<td>Sample 2</td>
<td>771</td>
<td>56</td>
<td>0.471</td>
<td>33.72</td>
</tr>
</tbody>
</table>

Table 6.10 (a): Trial 3.1 Results

<table>
<thead>
<tr>
<th></th>
<th>Filterability Test (ml/min.)</th>
<th>Test Temp. ($^\circ$C)</th>
<th>Calcium Citrate Assay (% Calcium Citrate)</th>
<th>M.P.S. (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control Sample</td>
<td>844</td>
<td>66</td>
<td>0.440</td>
<td>46.21</td>
</tr>
<tr>
<td>Sample 1</td>
<td>1122</td>
<td>62</td>
<td>0.463</td>
<td>44.77</td>
</tr>
<tr>
<td>Sample 2</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>45.30</td>
</tr>
</tbody>
</table>

Table 6.10 (b): Trial 3.2 Results

<table>
<thead>
<tr>
<th></th>
<th>Filterability Test (ml/min.)</th>
<th>Test Temp. ($^\circ$C)</th>
<th>Calcium Citrate Assay (% Calcium Citrate)</th>
<th>M.P.S. (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control Sample</td>
<td>900</td>
<td>56</td>
<td>---</td>
<td>52.15</td>
</tr>
<tr>
<td>Sample 1</td>
<td>1125</td>
<td>57</td>
<td>---</td>
<td>54.92</td>
</tr>
<tr>
<td>Sample 2</td>
<td>1227</td>
<td>56</td>
<td>---</td>
<td>55.59</td>
</tr>
</tbody>
</table>

Table 6.10 (c); Trial 3.3 Results

Trial numbers 3.2 and 3.3 suggested a slight improvement in filterability results. The mean particle sizes also showed a slight improvement in trial no. 3.3. However, the insignificance of the size increase is clearly visible from an overlay plot of the size distributions given in Figure 6.7.
**Conclusions:**

Overall, although a slight improvement in mean particle size and filterability results was observed, these improvements were not significant enough to warrant further investigation.

### 6.5.4 Investigation 4: Hemihydrate Production

**Objective:**

Verify the conditions required for hemihydrate production.

**Procedure:**

Experimental runs were carried out with a view to producing hemihydrate as opposed to the normally desired dihydrate gypsum. This was achieved by operating at a low agitation speed (initially set at 60% of the maximum, but later needed to be increased in order to mix the reactor contents) and also at a high $\text{H}_2\text{SO}_4$ (96% w/w) flowrate. These conditions created the normally undesirable ‘hot-spots’ within the reactor. 240 mls of $\text{H}_2\text{SO}_4$ was added (excess acid) and a sample was taken. After a 2 hour residence time period, the remainder of the acid in the feed...
container was added to achieve ‘product burning’. The reactor contents turned a strong creamy/grey colour and also appeared more viscous. A sample of this material was then taken.

In a second trial, 380 mls of H₂SO₄ was added to the reactor and a sample taken after 30 minutes. After a 2 hour residence time period, a further sample was taken. At this stage, the slurry had turned the strong creamy/grey colour as experienced during the previous trial.

**Results:**

The filterability results and mean particle sizes of the samples are given in Table 6.11 and the results of the solids analysis is given in Table 6.12.

<table>
<thead>
<tr>
<th></th>
<th>Filterability Test (ml/min.)</th>
<th>Test Temp. (°C)</th>
<th>M.P.S. (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control Sample</td>
<td>882</td>
<td>67</td>
<td>37.85</td>
</tr>
<tr>
<td>Sample 1</td>
<td>566</td>
<td>67</td>
<td>40.44</td>
</tr>
<tr>
<td>Sample 2</td>
<td>&lt;17</td>
<td>67</td>
<td>5.67</td>
</tr>
</tbody>
</table>

Table 6.11: Filterability and Malvern Results from Trial No. 4.1.

<table>
<thead>
<tr>
<th></th>
<th>Slurry</th>
<th>Filtrate</th>
<th>% Grey Layer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control Sample</td>
<td>67</td>
<td>0.2</td>
<td>~0.13</td>
</tr>
<tr>
<td>Sample 1</td>
<td>70</td>
<td>0.4</td>
<td>~0.30</td>
</tr>
<tr>
<td>Sample 2</td>
<td>71</td>
<td>&gt;1.5</td>
<td>~1.35</td>
</tr>
</tbody>
</table>

Table 6.12: Solids Analysis - Trial No. 4.1

**Analysis and Discussion of Results:**

The filterability of the initial laboratory sample was reasonably lower than the control sample while the second laboratory sample showed a dramatic change in the filterability. After 40 minutes, 500 mls of the slurry had not filtered completely. This suggested severe blinding of the filter cloth by the slurry material.

Although the mean particle size of the first sample was slightly larger than the control sample, the microscopic analysis illustrated a higher quantity of ‘black’ microcrystalline material (characteristic of the hemihydrate formation) in the laboratory sample than in the control sample (see Figure 6.8).

The histogram reports suggested that the change in distribution occurred between approximately 15μm and 60μm with no change in the upper and lower ends of the distribution.
From the laboratory sample, almost 90% of the distribution was found to be larger than 10\(\mu\)m and approximately 44% of the distribution lay above 45\(\mu\)m. The second laboratory sample illustrated large quantities of this 'black' material in the microscopic analysis (see Figure 6.9) which was further supported by the Malvern result.

The mean particle size was found to be 5.67\(\mu\)m with only approximately 40% of the particles larger than 10\(\mu\)m versus approximately 90% from the first laboratory sample. Particles with sizes as low as 0.061\(\mu\)m were present in this distribution while 0.635\(\mu\)m was the smallest particle detected in the control sample. A clear distinction can be made between the desired dihydrate gypsum (Figure 4.7) and the undesired hemihydrate gypsum shown in Figures 6.8 and 6.9 above.

Similarly for the second trial, the first laboratory sample gave a distribution with 85% of the particles greater than 10\(\mu\)m and 50% greater than 45\(\mu\)m. The creamy/grey slurry gave a mean particle size of 2.97\(\mu\)m with only 2.5% of the entire distribution larger than 10\(\mu\)m. The filterability test on this sample showed that most of the sample went right through the filter.
cloth and very little cake was retained. This phenomenon was explained by the size of the particles. This observation was in contrast to that from the first trial where blinding of the filter cloth took place. However, the particle size distributions showed a significant difference between both trials (approximately 40% of the distribution was larger than 10\(\mu\)m in trial number 4.1 while only approximately 2.5% of the distribution was larger than 10\(\mu\)m in trial number 4.2). Therefore, the quantity of particles large enough to be retained on the filter in trial number 4.2 was sufficient to cause blinding of the filter cloth to the smaller particles.

The solids content of the slurry samples did not vary much between the control and test samples. However, the filtrate samples showed a considerable difference in the solids content. As expected, the solids content increased with the production of hemihydrate gypsum, in particular with the second laboratory sample. The grey layer indicated the presence of hemihydrate and was seen to increase dramatically after the ‘product burning’ had taken place.

**Conclusions:**

These trials resulted in the successful formation of microcrystalline hemihydrate material. This was achieved by the use of high \(\text{H}_2\text{SO}_4\) flowrates and low agitation speeds to create ‘hot-spots’ within the reactor and an excess quantity of acid was used to cause ‘product burning’. The combination of these conditions to produce the microcrystalline material verified the required conditions for this production. The filtration of the slurry proved that the material is capable of getting through the filter cloth which, in the plant scale, would then be undesirably present in the refining end. A high possibility of filter cloth blinding also exists which is detrimental to the gypsum filtration step.

Overall, the trials demonstrated the conditions which should be avoided in the plant at all times in an effort to eliminate the production of hemihydrate gypsum. The resulting effects of the undesirable conditions were also clearly illustrated.
6.5.5 Investigation 5: Reaction of Calcium Citrate Cake and H$_2$SO$_4$

**Objective:**
Determine the effect of reacting H$_2$SO$_4$ directly with calcium citrate cake.

**Procedure:**
Calcium citrate cake was taken from the plant calcium citrate second stage filter. The stoichiometric amount of H$_2$SO$_4$ (96% w/w) required to convert the calcium citrate to gypsum was added dropwise to the cake and a sample taken. An excess of the stoichiometric amount of H$_2$SO$_4$ was then added to create a less viscous slurry and a second sample was taken.

**Analysis and Discussion:**
The resulting crystals were very small needle-shaped crystals and are shown in Figure 6.10. These small crystals are undesirable for filtration due to their poor filterability. When more than the stoichiometric amount of acid was added, hemihydrate gypsum was produced (Section 6.5.4). During the trial, the addition of H$_2$SO$_4$ caused the product to release a significant amount of heat. Due to the fact that the H$_2$SO$_4$ was added directly onto the cake and not below the surface of a slurry, the cake began to spit and splash when contacted with the acid.

![Figure 6.10: Small Needle-Shaped Crystals](image)

**Conclusions:**
The laboratory reaction of H$_2$SO$_4$ with calcium citrate cake produced poor quality crystals which would be difficult to filter and wash. The physical nature of the slurry also suggested handling difficulties. From a safety view-point, this reaction mechanism would not be feasible on a large scale due to the heat generation and 'spitting' nature of the cake on contact with the acid.
acid. The difficulty in generating a slurry with acceptable agitating and pumping characteristics would also pose a problem in the large scale. Overall, this trial emphasised the necessity of the reaction to take place in a slurry form, with the $\text{H}_2\text{SO}_4$ added below the surface.

6.5.6 Investigation 6: Reaction of Calcium Citrate Slurry and $\text{H}_2\text{SO}_4$

Objective:
Investigate the reaction between $\text{H}_2\text{SO}_4$ and calcium citrate slurry taken from the final calcium citrate reaction vessel [i.e prior to the calcium citrate filtration and reslurrying stage]

Procedure:
Calcium citrate slurry was taken from the final calcium citrate reaction vessel and reacted with 96% w/w $\text{H}_2\text{SO}_4$. This reaction involved decomposing the calcium citrate to gypsum in the presence of the citric acid mother liquor and in the absence of gypsum recycle from the strike tank. The slurry was pumped to the reactor and the $\text{H}_2\text{SO}_4$ was added to give a pH of approximately 0.9. Due to the lower viscosity of the slurry, a lower agitation speed was used. The reaction mixture turned a very dark brown colour during the reaction. Three trials were carried out using the calcium citrate slurry. A fourth trial was carried out using a higher solids content in the slurry by adding calcium citrate cake to the slurry.

Results:
The results obtained from these trials are given in Table 6.13.

<table>
<thead>
<tr>
<th></th>
<th>Filterability Test (ml/min.)</th>
<th>Test Temp. ($^\circ$C)</th>
<th>$D(v,0.5)$ ($\mu$m)</th>
<th>$D(v,0.9)$ ($\mu$m)</th>
<th>$D(v,0.1)$ ($\mu$m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control 6.1</td>
<td>909</td>
<td>66</td>
<td>46.65</td>
<td>100.75</td>
<td>11.29</td>
</tr>
<tr>
<td>Trial 6.1</td>
<td>—</td>
<td>—</td>
<td>64.67</td>
<td>131.40</td>
<td>13.26</td>
</tr>
<tr>
<td>Control 6.2/6.4</td>
<td>882</td>
<td>66</td>
<td>48.04</td>
<td>99.80</td>
<td>11.72</td>
</tr>
<tr>
<td>Trial 6.2</td>
<td>3333</td>
<td>66</td>
<td>84.56</td>
<td>165.60</td>
<td>17.10</td>
</tr>
<tr>
<td>Trial 6.4</td>
<td>2727</td>
<td>66</td>
<td>114.34</td>
<td>191.13</td>
<td>42.21</td>
</tr>
<tr>
<td>Control 6.5</td>
<td>882</td>
<td>62</td>
<td>44.03</td>
<td>91.05</td>
<td>11.25</td>
</tr>
<tr>
<td>Trial 6.5</td>
<td>3333</td>
<td>65</td>
<td>47.06</td>
<td>383.50</td>
<td>11.98</td>
</tr>
<tr>
<td>Trial 6.5</td>
<td>—</td>
<td>—</td>
<td>62.53</td>
<td>140.90</td>
<td>16.56</td>
</tr>
</tbody>
</table>

Table 6.13: Filterability and Malvern Results
Analysis and Discussion of Results:

From Table 6.13 above, it is obvious that a significant improvement in filterability and particle size was achieved during these trials. [Note: due to a lower specific gravity in the gypsum slurry, the filterability results could not be adequately compared to the normal results but are included here for completion]. The filtration took place so rapidly, the filter cloth dried almost immediately after the slurry had been added to the filter.

The microscopic analysis illustrated plate-like parallelogram shaped crystals of gypsum and the distribution of particles seemed to be much more uniform. These good quality crystals would have better filtration characteristics to the gypsum crystals being produced currently. Photographic evidence of the improved crystals is given in Figures 6.11 and 6.12 below.

Figure 6.11: Gypsum Crystals

Figure 6.12: Gypsum Crystals

The solids content of the resulting gypsum slurry was found to be much lower than the normal plant gypsum slurry. However, the solids content of the initial reactant slurry was also lower than the slurry normally used. The slurry from the last calcium citrate reaction vessel has a solids content of only approximately 40%, in comparison to the normal reactant slurry (solids content approximately 70%). To investigate the reduced solids in the resulting gypsum slurry,
additional quantities of calcium citrate cake were added to the calcium citrate slurry for trial number 6.5 to give a solids content of approximately 60% in the reactant slurry. Analysis of the solids content again only yielded a low solids content (17%) in the gypsum slurry as opposed to 66% in the control sample. Therefore, additional solids in the reactant slurry did not increase the solids content in the final mixture.

Conclusions:

These trials suggested significant improvements in the crystals and therefore improved filtration rates. Plate-like parallelogram-shaped crystals of gypsum were formed and the filterability result appeared to be much improved on the control samples. Overall, this investigation indicated that reaction of the calcium citrate to gypsum in the presence of the citric acid mother liquor, gave promising results with a view to the development of a possible solution to the plant gypsum filtration problems.

6.5.7 Investigation 7: Reaction of Calcium Citrate Cake (Slurried in Sour Filtrate) and H₂SO₄

Objective:

Investigate the reaction between H₂SO₄ and calcium citrate cake slurried in sour filtrate from the pannevis as a follow-up to the investigation described in Section 6.5.6.

Procedure:

Calcium citrate cake from the calcium citrate filters was slurried with the very strong filtrate from the pannevis filter (see Section 3.2.8). The slurry was made up to contain approximately 65% solids in the slurry. This slurry was then reacted with 96% w/w H₂SO₄ to form gypsum.

Analysis and Discussion of Results:

The mean particle size of the gypsum formed was 43.73μm which was no improvement over the gypsum normally produced. The filterability result was also poor (545 ml/min. @ test temperature of 64°C).
Conclusion:
The presence in the reaction, of citric acid mother liquor from the pannevis very strong filtrate, did not have the same improved effect on the gypsum crystals as the calcium citrate slurry reaction (see Section 6.5.6). This suggested that some impurity present in the citric acid liquor prior to the calcium citrate filtration stage (but not present in the liquor remaining after the pannevis filtration), had an effect on the crystals in the previous experiment.

6.5.8 Investigation 8: Reaction with Calcium Citrate Cake Slurried in H₂O

Objective:
Investigate the reaction between H₂SO₄ and calcium citrate cake slurried in water.

Procedure:
Calcium citrate cake was slurried in water and poured into the reactor. H₂SO₄ (96% w/w) was added to bring the pH close to the strike tank pH value. Some of the reaction mixture was then removed, more calcium citrate added, followed by more H₂SO₄. This procedure was repeated to bring the specific gravity of the slurry close to that of the plant. Agitation in the reactor appeared difficult at times. Although the slurry specific gravities at the sample times were slightly lower than desired, the trial samples were accepted. Calcium citrate assays on the samples confirmed full conversion of the calcium citrate to gypsum. Since the vortex mixer was off-line during these trials, the solids content of both the control and trial samples were analysed to verify that less hemihydrate gypsum was formed in the laboratory.

Results:
The results obtained from these trials are given in Tables 6.14 and 6.15.

<table>
<thead>
<tr>
<th></th>
<th>Filterability Test</th>
<th>Test Temp.</th>
<th>D(v,0.5) (μm)</th>
<th>D(v,0.9) (μm)</th>
<th>D(v,0.1) (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control 8.1</td>
<td>1500</td>
<td>---</td>
<td>60.80</td>
<td>136.17</td>
<td>11.81</td>
</tr>
<tr>
<td>Trial 8.1</td>
<td>3750</td>
<td>---</td>
<td>34.02</td>
<td>77.01</td>
<td>6.80</td>
</tr>
<tr>
<td>Control 8.2</td>
<td>1250</td>
<td>---</td>
<td>65.72</td>
<td>171.99</td>
<td>12.78</td>
</tr>
<tr>
<td>Trial 8.2</td>
<td>3750</td>
<td>---</td>
<td>33.57</td>
<td>70.95</td>
<td>8.03</td>
</tr>
<tr>
<td>Control 8.3</td>
<td>2000</td>
<td>---</td>
<td>68.55</td>
<td>160.21</td>
<td>11.60</td>
</tr>
<tr>
<td>Trial 8.3</td>
<td>2308</td>
<td>---</td>
<td>31.92</td>
<td>65.69</td>
<td>7.83</td>
</tr>
</tbody>
</table>

Table 6.14: Filterability and Malvern Results
### Table 6.15: Solids Analysis

<table>
<thead>
<tr>
<th>Slurry</th>
<th>Total % Solids</th>
<th>Filtrate</th>
<th>Total % Solids</th>
<th>% Grey Layer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control 8.1</td>
<td>64</td>
<td></td>
<td>0.500</td>
<td>~ 0.400</td>
</tr>
<tr>
<td>Trial 8.1</td>
<td>57</td>
<td></td>
<td>0.275</td>
<td>~ 0.070</td>
</tr>
<tr>
<td>Control 8.2</td>
<td>65</td>
<td></td>
<td>0.500</td>
<td>~ 0.400</td>
</tr>
<tr>
<td>Trial 8.2</td>
<td>66</td>
<td></td>
<td>0.250</td>
<td>~ 0.075</td>
</tr>
<tr>
<td>Control 8.3</td>
<td>67</td>
<td></td>
<td>0.550</td>
<td>~ 0.370</td>
</tr>
<tr>
<td>Trial 8.3</td>
<td>69</td>
<td></td>
<td>0.200</td>
<td>~ 0.070</td>
</tr>
</tbody>
</table>

**Analysis and Discussion of Results:**

The mean particle sizes of the trial samples were much smaller than the plant control samples. The 10% and 90% points also showed smaller values which suggested an overall shift in the distribution from right to left. This shift in distribution can be seen from the Malvern overlay plot in Figure 6.13.

![Malvern Overlay Plot](image)

The microscopic analysis illustrated more needle-shaped crystals as opposed to the "normal" criss-cross / plate-like crystals obtained. The filterability results appeared to be much improved in Trials 8.1 and 8.2 which is contradictory to the Malvern results. However, this can be explained by the fact that the slurry specific gravities at the sample times were lower than the desired target specific gravity values. In trial 8.3, the actual specific gravity was closer to the...
target value and it was evident from the filterability results that the improvement was not as significant.

The solids results from the plant samples were found to be quite high with approximately two-thirds of the total solids content in the filtrate being hemihydrate. This was due to the plant vortex mixer being off-line during the trials. As expected, the laboratory reaction gave improved solids results with smaller quantities of hemihydrate present.

Conclusions:

Overall, the reaction mechanism using water to slurry the calcium citrate cake produced smaller crystals. Although enhanced filtration rates were experienced during trials 8.1 and 8.2, this was due to the lower specific gravities of the laboratory slurries.

6.5.9 Investigation 9: Reaction using Calcium Citrate Cake Slurried in Filtrate from the Calcium Citrate Filtration Step

Objective:

Investigate if the improved results described in Section 6.5.6 can be achieved by reaction of sulphuric acid with the calcium citrate cake slurried in filtrate from the calcium citrate filtration step. Then compare the results to those obtained from slurrying the cake in water and repeating the reaction.

Procedure:

Calcium citrate cake was taken from the 1st stage calcium citrate filter. Filtrate from the same filtration step was used to reslurry the cake. Sulphuric acid was then added to the slurry to convert the calcium citrate to gypsum. Approximately 350g of calcium citrate was slurried in about 4 litres of filtrate for trials 9.1 and 9.2. This gave a slurry with low solids content and hence low specific gravity. For the third trial, 2000g of calcium citrate cake was slurried in 3 litres of the filtrate. This gave a slurry with a specific gravity close to that of the slurry used in the plant for the gypsum reaction.
Results:
The results obtained from these trials are given in Table 6.16. The main emphasis during these particular trials was on particle size measurement. Hence, the results tabulated here are the mean particle sizes along with the 90% and 10% cut-off points. Note, a control sample was only taken for trial 9.1. However, the particle size of the plant gypsum was typically in the 40-60μm size range and based on this, the trial samples could be adequately assessed for any improvements.

<table>
<thead>
<tr>
<th></th>
<th>Control 9.1</th>
<th>Trial 9.1</th>
<th>Trial 9.2</th>
<th>Trial 9.3</th>
</tr>
</thead>
<tbody>
<tr>
<td>D(v, 0.5) (μm)</td>
<td>59.27</td>
<td>102.91</td>
<td>127.79</td>
<td>41.69</td>
</tr>
<tr>
<td>D(v, 0.9) (μm)</td>
<td>132.30</td>
<td>199.23</td>
<td>287.56</td>
<td>123.78</td>
</tr>
<tr>
<td>D(v,0.1) (μm)</td>
<td>11.02</td>
<td>22.66</td>
<td>16.29</td>
<td>8.75</td>
</tr>
</tbody>
</table>

Table 6.16: Malvern Particle Size Results

Analysis and Discussion of Results:
From Table 6.16, it is obvious that a significant improvement in particle size was achieved in trials 9.1 and 9.2. For trial 9.3 however, the mean particle size was in the typical size range for the gypsum crystals. The 90% cut-off points showed a dramatic shift to the right at the upper end of the distribution. An improvement in the lower end of the distribution was also observed. The microscopic analysis also supported the Malvern results with higher quality crystals achieved during trials 9.1 and 9.2 than were obtained from trial 9.3. These results suggested that the difference in specific gravity of the reactant slurry had a significant effect on the resulting crystal size. The more dilute slurries gave a much better crystal appearance as well as mean particle sizes of over double those obtained in the plant.

Conclusions:
On evaluation of the results from trials 9.1 and 9.2, the microscopic analysis clearly illustrated that much better crystals were achieved when the reaction took place in the presence of the filtrate from the dical filtration step. This result was in agreement with that described in Section 6.5.6. The Malvern analysis also supported the microscopic evidence of improved crystal size with mean particle sizes of approximately double the control values achieved. These trials, combined with the trial using filtrate from the pannevis filtration step, suggested that some
impurity removed at the calcium citrate filtration stage had a beneficial effect on the gypsum crystals. However, trial 9.3 rejected this theory while suggesting that the improved crystals obtained in trials 9.1 and 9.2 were as a result of a much lower slurry specific gravity. The experiment described in Section 6.5.7 where the calcium citrate cake was slurried in the pannevis filtrate, involved preparation of a slurry to give approximately 65% solids in the slurry. This slurry therefore had a high specific gravity and showed no improvement in crystal size or appearance, in agreement with trial 9.3 in this case.

6.5.10 Investigation 10: Reaction using Calcium Citrate Cake Slurried in Water in the presence of Potassium & Sodium Citrate as Impurities

Background:
After completion of trials described in Sections 6.5.6 and 6.5.7, it was thought that some impurity present in the calcium citrate slurry and then removed at the calcium citrate filtration stage had a beneficial effect on the gypsum crystals. The impurities present in the largest quantities prior to the calcium citrate filtration step are potassium and sodium and are present in the form of potassium citrate and sodium citrate. Reactions were therefore carried out using calcium citrate cake slurried in water in the presence of both of these impurities.

Objective:
Identify the impurity having a positive influence on the gypsum crystals.

Procedure:
350g of calcium citrate cake was slurried in 4 litres of water containing 2.5 wt.% Potassium Citrate and 0.5 wt.% Sodium Citrate. Sulphuric acid was added to produce gypsum. The experiment was repeated with 2.5 wt.% Potassium Citrate alone in the water followed by an experiment with 0.5 wt.% Sodium Citrate alone in the water.

Results:
The particle size results obtained from the three trials are given in Table 6.17
Table 6.17: Malvern Particle Size Results

<table>
<thead>
<tr>
<th>Trial No.</th>
<th>D(v,0.5) (µm)</th>
<th>D(v,0.9) (µm)</th>
<th>D(v,0.1) (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.1</td>
<td>107.18</td>
<td>228.68</td>
<td>9.54</td>
</tr>
<tr>
<td>10.2</td>
<td>61.19</td>
<td>146.87</td>
<td>10.47</td>
</tr>
<tr>
<td>10.3</td>
<td>93.40</td>
<td>174.75</td>
<td>26.51</td>
</tr>
</tbody>
</table>

Analysis and Discussion of Results:

Trial 10.1 gave a gypsum mean particle size of 107µm with 10% of the distribution lying above 229µm and 10% below 9.5µm. The microscopic analysis illustrated large rectangular-shaped crystals. The presence of potassium citrate alone in trial 10.2 produced parallelogram-shaped crystals (see Figure 6.14) with a mean particle size of 61µm (90% of the distribution lay below 147µm while 10% lay below 10.5µm). The experiment with just 0.5 wt.% sodium citrate in the water gave a majority of rectangular-shaped crystals (see Figure 6.15). The mean particle size was found to be 93µm with 10% of the distribution above 175µm and only 10% below 26µm.
Conclusion:
From these experiments it appeared that both Sodium and Potassium Citrate had a positive
influence on the gypsum crystals. Although the Malvern results were found to be relatively
normal with the Potassium Citrate alone, the crystals appeared much better than the usual
gypsum crystals. The difference in Malvern results between this and the other experiments
was explained by the actual shape of the crystals. The longitudinal axis appeared longer in the
presence of Sodium Citrate which would explain the larger Malvern results. The volume of
particles in the tail of the distribution appeared smaller in the experiment with Sodium Citrate
alone (only 10% of particles smaller than 26μm). Overall, the presence of Potassium Citrate
and/or Sodium Citrate in the reaction from calcium citrate to gypsum appeared to have a
positive influence on the gypsum crystals.

6.5.11  Investigation 11: Dilution Trials

Background:
Following the results of trial 9.3 (Section 6.5.9), a further series of experiments were
performed to verify that low specific gravity (or high dilution) was the reason for improved
crystals as described in sections 6.5.6, 6.5.9 and 6.5.10. Although some experiments
described in previous sections were repeated in this experimental series, the repetition was
necessary to determine the exact cause of the crystal improvements.

Objective:
Verify that dilution improves the gypsum crystals

Procedure:
A series of experiments was performed with varying amounts of calcium citrate, water and
impurities used. Sulphuric acid was added to the reactant slurry to give a pH of approximately
0.9 in each case. The exact quantities of reagents used for each trial are listed with the results
given in Table 6.18.
Results:

<table>
<thead>
<tr>
<th>Trial No.</th>
<th>Mass Calc. Cit. Cake (g)</th>
<th>Vol. H₂O (mls)</th>
<th>Ratio (H₂O: Cake)</th>
<th>Mass Na.Cit. (g)</th>
<th>Specific Gravity</th>
<th>D(ν,0.5) (μm)</th>
<th>D(ν,0.9) (μm)</th>
<th>D(ν,0.1) (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>11.1</td>
<td>2000</td>
<td>2700</td>
<td>1.35</td>
<td>6</td>
<td>1134</td>
<td>43.44</td>
<td>138.95</td>
<td>9.53</td>
</tr>
<tr>
<td>11.2</td>
<td>2000</td>
<td>2000</td>
<td>1.00</td>
<td>12</td>
<td>1170</td>
<td>43.61</td>
<td>182.28</td>
<td>11.21</td>
</tr>
<tr>
<td>11.3</td>
<td>400</td>
<td>3200</td>
<td>8.00</td>
<td>12</td>
<td>1040</td>
<td>100.75</td>
<td>269.01</td>
<td>11.28</td>
</tr>
<tr>
<td>11.4</td>
<td>400</td>
<td>3200</td>
<td>8.00</td>
<td>2.4</td>
<td>1050</td>
<td>99.84</td>
<td>243.84</td>
<td>11.96</td>
</tr>
<tr>
<td>11.5</td>
<td>400</td>
<td>3200</td>
<td>8.00</td>
<td>--</td>
<td>1042</td>
<td>104.81</td>
<td>196.21</td>
<td>17.53</td>
</tr>
<tr>
<td>11.6</td>
<td>2000</td>
<td>2700</td>
<td>1.35</td>
<td>80</td>
<td>1160</td>
<td>52.17</td>
<td>178.17</td>
<td>11.29</td>
</tr>
<tr>
<td>11.7</td>
<td>400</td>
<td>3200</td>
<td>8.00</td>
<td>--</td>
<td>1040</td>
<td>106.50</td>
<td>211.43</td>
<td>19.23</td>
</tr>
<tr>
<td>11.8</td>
<td>2000</td>
<td>2500</td>
<td>6.25</td>
<td>--</td>
<td>1200</td>
<td>28.21</td>
<td>84.09</td>
<td>6.74</td>
</tr>
<tr>
<td>11.9</td>
<td>400</td>
<td>2500</td>
<td>6.25</td>
<td>--</td>
<td>1050</td>
<td>72.18</td>
<td>179.10</td>
<td>10.51</td>
</tr>
<tr>
<td>11.10</td>
<td>400</td>
<td>3200</td>
<td>8.00</td>
<td>--</td>
<td>--</td>
<td>56.22</td>
<td>110.57</td>
<td>10.96</td>
</tr>
<tr>
<td>11.11</td>
<td>400</td>
<td>3200</td>
<td>8.00</td>
<td>2.4</td>
<td>--</td>
<td>63.52</td>
<td>129.22</td>
<td>13.35</td>
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<tr>
<td>11.12</td>
<td>400</td>
<td>3200</td>
<td>8.00</td>
<td>12</td>
<td>--</td>
<td>65.34</td>
<td>125.98</td>
<td>12.16</td>
</tr>
<tr>
<td>11.13</td>
<td>400</td>
<td>3200</td>
<td>8.00</td>
<td>24</td>
<td>--</td>
<td>67.22</td>
<td>127.19</td>
<td>11.33</td>
</tr>
</tbody>
</table>

Table 6.18: Dilution Trial Results

Analysis and Discussion of Results:

From the results shown in Table 6.18, it is evident that the improved particle size results were achieved at low specific gravities (i.e. when the ratio of water to calcium citrate cake was high - indicated by shading in Table 6.18). When experiments were carried out at specific gravities in the range of 1130 - 1200, the particle size results were found to be similar to the existing plant results. This verifies that the improved crystal size and appearance described in Sections 6.5.6, 6.5.9 and 6.5.10 was a result of dilution and not due to some impurity present in the slurry as previously suggested.

Conclusion:

These experiments verified that with a high dilution factor, improvements in crystal size and overall crystal appearance could be obtained. The theories previously suggested regarding a positive influence by some impurity in the system have now been eliminated.
6.5.12 Influence of Impurities

6.5.12.1 Introduction

The citric acid broth entering the recovery area of the plant from fermentation contains both soluble and insoluble impurities such as K, Mg, Na, Fe, Cl, etc. The impurity contents in the citric broth at various stages of the citric acid production process is analysed on a monthly basis. A composite sample collected over a one month period is used for the analysis. The concentrations of these impurities vary throughout the process due to concentration or dilution of the broths, as a result of evaporation or washing. In order to determine the influence (if any) of these impurities on the gypsum formation step, additional quantities of the cationic impurities were added to the reaction mixture. The reagents added were:

- potassium sulphate $\text{K}_2\text{SO}_4$
- sodium sulphate $\text{Na}_2\text{SO}_4\cdot10\text{H}_2\text{O}$
- magnesium sulphate $\text{MgSO}_4\cdot7\text{H}_2\text{O}$
- iron (II) sulphate $\text{FeSO}_4\cdot7\text{H}_2\text{O}$
- iron (III) sulphate $\text{Fe}_2\text{(SO}_4)_3\cdot\text{xH}_2\text{O}$
- aluminium sulphate $\text{Al}_2\text{(SO}_4)_3\cdot16\text{H}_2\text{O}$

From the literature survey outlined in chapter 2, iron (III) sulphate and aluminium sulphate both had a positive influence on the gypsum crystals in phosphoric acid production (Hasson et al., 1990). Hence, the effect of these impurities on the production of gypsum was examined.

Objective: Investigate the effect of the presence of $\text{K}_2\text{SO}_4$ in the reaction mixture.

Procedure:

Various quantities of $\text{K}_2\text{SO}_4$ were dissolved in 96% w/w $\text{H}_2\text{SO}_4$. The solution concentrations tested were 0.05, 0.1, 0.3 and 1.0 mol $\text{K}_2\text{SO}_4$ per litre of $\text{H}_2\text{SO}_4$. These $\text{H}_2\text{SO}_4$ solutions were reacted with slurry from the calcium citrate filter repulper to form gypsum. Each trial was defined as in Table 6.19.
Chapter Six - Laboratory Investigations

Moles of Impurity per litre $\text{H}_2\text{SO}_4$

<table>
<thead>
<tr>
<th>Trial</th>
<th>Impurity Mass (g) per 250mls $\text{H}_2\text{SO}_4$</th>
<th>% w/v of Impurity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Trial 12.1</td>
<td>0.05</td>
<td>2.178</td>
</tr>
<tr>
<td>Trial 12.2</td>
<td>0.10</td>
<td>4.357</td>
</tr>
<tr>
<td>Trial 12.3</td>
<td>0.30</td>
<td>13.070</td>
</tr>
<tr>
<td>Trial 12.4</td>
<td>1.00</td>
<td>43.568</td>
</tr>
</tbody>
</table>

Table 6.19: $\text{K}_2\text{SO}_4$ Impurity Trial Details

Results: The trial results are summarised in Table 6.20.

<table>
<thead>
<tr>
<th>D(v,0.5) (microns)</th>
<th>Filterability (ml/min.)</th>
<th>Test Temp ($^\circ$C)</th>
<th>Total Solids Content of Filtrate (%)</th>
<th>% Hemi-hydrate</th>
<th>A.A. Results (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control 12.1</td>
<td>45.09</td>
<td>680</td>
<td>60</td>
<td>0.2</td>
<td>0.1</td>
</tr>
<tr>
<td>Trial 12.1</td>
<td>48.92</td>
<td>860</td>
<td>60</td>
<td>0.2</td>
<td>0.1</td>
</tr>
<tr>
<td>Control 12.1</td>
<td>44.88</td>
<td>770</td>
<td>69</td>
<td>----</td>
<td>----</td>
</tr>
<tr>
<td>Trial 12.1</td>
<td>43.19</td>
<td>860</td>
<td>68</td>
<td>----</td>
<td>----</td>
</tr>
<tr>
<td>Control 12.2</td>
<td>54.42</td>
<td>485</td>
<td>47</td>
<td>0.350</td>
<td>0.300</td>
</tr>
<tr>
<td>Trial 12.2</td>
<td>53.64</td>
<td>460</td>
<td>47</td>
<td>0.225</td>
<td>0.175</td>
</tr>
<tr>
<td>Control 12.3</td>
<td>45.12</td>
<td>770</td>
<td>60</td>
<td>0.2</td>
<td>0.1</td>
</tr>
<tr>
<td>Trial 12.3</td>
<td>44.74</td>
<td>800</td>
<td>58</td>
<td>0.2</td>
<td>0.1</td>
</tr>
<tr>
<td>Control 12.4</td>
<td>45.09</td>
<td>680</td>
<td>60</td>
<td>0.2</td>
<td>0.1</td>
</tr>
<tr>
<td>Trial 12.4</td>
<td>48.62</td>
<td>830</td>
<td>60</td>
<td>0.2</td>
<td>0.1</td>
</tr>
<tr>
<td>Control 12.4</td>
<td>44.88</td>
<td>770</td>
<td>69</td>
<td>----</td>
<td>----</td>
</tr>
<tr>
<td>Trial 4</td>
<td>44.92</td>
<td>830</td>
<td>67</td>
<td>----</td>
<td>----</td>
</tr>
</tbody>
</table>

Table 6.20: $\text{K}_2\text{SO}_4$ Impurity Trial Results

Repeat of Trials 12.1 and 12.4

Analysis and Discussion of Results:

The mean particle size results for trials 12.1 and 12.4 showed a slight increase from the control sample to the test sample. The filterability results also suggested an improvement. However, on repeat of these trials, the difference between the samples was not found to be significant. This was in agreement with the results found for trials 12.2 and 12.3 where the mean particle sizes did not change significantly between the control and test samples. The filterability results of the test samples also showed little improvement over the control samples. Analysis of the solids content in the filtrates showed no difference between the test and control samples for trials 12.1, 12.3, and 12.4. A slight difference in solids content was evident for trial 12.2. This may have been due to a blockage in the vortex mixer leading to possible hot-spot formation. The atomic absorption results indicated the increasing quantities of impurity in the
filtrate as the quantities of K$_2$SO$_4$ added were increased from the control to test samples. This analysis also verified that the potassium remained in solution after the reaction to gypsum had taken place.

**Conclusions:**

The overall conclusion from these trials is that the addition of K$_2$SO$_4$ did not influence the gypsum crystals. The mean particle sizes remained practically unchanged and any fluctuations in the filtration rates were not significant. Since the potassium remained in the citric acid solution after the conversion to gypsum had taken place, increase of the impurity concentration above the concentrations tested, did not seem practical.

**Objective:** Investigate the effect of the presence of Na$_2$SO$_4$.10H$_2$O in the reaction mixture.

**Procedure:**

Various quantities of Na$_2$SO$_4$.10H$_2$O were dissolved in 96% w/w H$_2$SO$_4$. The solution concentrations tested were 0.02, 0.05, 0.1 and 0.5 mol Na$_2$SO$_4$.10H$_2$O per litre of H$_2$SO$_4$. These H$_2$SO$_4$ solutions were reacted with slurry from the calcium citrate filter repulper to form gypsum. Solubility of the impurity in H$_2$SO$_4$ was difficult at the higher concentrations. Therefore, two trials were carried out where the impurity was added directly to the reactor in solid form. Each trial is defined as follows:

<table>
<thead>
<tr>
<th>Trial</th>
<th>Moles of Impurity per litre H$_2$SO$_4$</th>
<th>Mass Impurity (g) per 250mls H$_2$SO$_4$</th>
<th>% w/v of Impurity</th>
</tr>
</thead>
<tbody>
<tr>
<td>12.5</td>
<td>0.020</td>
<td>2.178</td>
<td>0.87</td>
</tr>
<tr>
<td>12.6</td>
<td>0.050</td>
<td>4.357</td>
<td>1.74</td>
</tr>
<tr>
<td>12.7</td>
<td>0.100</td>
<td>13.070</td>
<td>5.23</td>
</tr>
<tr>
<td>12.8</td>
<td>0.500</td>
<td>43.568</td>
<td>17.43</td>
</tr>
<tr>
<td>12.9</td>
<td>0.587</td>
<td>47.27</td>
<td>18.91</td>
</tr>
<tr>
<td>12.10</td>
<td>1.036</td>
<td>83.47</td>
<td>33.39</td>
</tr>
</tbody>
</table>

Table 6.21: Na$_2$SO$_4$.10H$_2$O Impurity Trial Details

**Results:**

The trial results are summarised in Table 6.22.
<table>
<thead>
<tr>
<th></th>
<th>$D(v,0.5)$ (microns)</th>
<th>Filterability (ml/min.)</th>
<th>Test Temp. ($^\circ$C)</th>
<th>Total Solids Content (%)</th>
<th>% Hemi-hydrate</th>
<th>A.A. Results (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control 12.5</td>
<td>46.95</td>
<td>715</td>
<td>66</td>
<td>0.150</td>
<td>0.100</td>
<td>10</td>
</tr>
<tr>
<td>Trial 12.5</td>
<td>44.98</td>
<td>750</td>
<td>66</td>
<td>0.150</td>
<td>0.100</td>
<td>40</td>
</tr>
<tr>
<td>Control 12.6</td>
<td>47.28</td>
<td>940</td>
<td>70</td>
<td>0.225</td>
<td>0.150</td>
<td>15</td>
</tr>
<tr>
<td>Trial 12.6</td>
<td>43.21</td>
<td>860</td>
<td>67</td>
<td>0.200</td>
<td>0.133</td>
<td>140</td>
</tr>
<tr>
<td>Control 12.7</td>
<td>46.95</td>
<td>715</td>
<td>66</td>
<td>0.150</td>
<td>0.100</td>
<td>10</td>
</tr>
<tr>
<td>Trial 12.7</td>
<td>43.54</td>
<td>560</td>
<td>67</td>
<td>0.150</td>
<td>0.100</td>
<td>280</td>
</tr>
<tr>
<td>Control 12.8</td>
<td>47.55</td>
<td>1000</td>
<td>64</td>
<td>0.200</td>
<td>—</td>
<td>20</td>
</tr>
<tr>
<td>Trial 12.8</td>
<td>51.68</td>
<td>1110</td>
<td>63</td>
<td>0.200</td>
<td>—</td>
<td>7200</td>
</tr>
<tr>
<td>Control 12.9</td>
<td>51.44</td>
<td>910</td>
<td>65</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Trial 12.9</td>
<td>47.07</td>
<td>810</td>
<td>65</td>
<td>—</td>
<td>—</td>
<td>1280</td>
</tr>
<tr>
<td>Control 12.10</td>
<td>47.56</td>
<td>960</td>
<td>65</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Trial 12.10</td>
<td>51.98</td>
<td>1000</td>
<td>63</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

Table 6.22: $\text{Na}_2\text{SO}_4.10\text{H}_2\text{O}$ Impurity Trial Results

**Analysis and Discussion of Results:**

The Malvern mean particle sizes indicated slight fluctuations (approximately 4μm) between the control and test results. For trials 12.5, 12.6, 12.7 and 12.9, the mean particle size was seen to decrease while an increase was observed in trials 12.8 and 12.10. The filterability tests also showed fluctuations, however in most cases a decrease in filtration rate was observed. The increase observed for trials 12.8 and 12.10 was not a significant improvement. The solids results illustrated no major change between the control and test samples. This was expected due to the vortex mixer being on line. The atomic absorption results served to illustrate the presence of the impurity in the filtrate solutions after the gypsum was removed.

**Conclusions:**

Overall, the addition of $\text{Na}_2\text{SO}_4.10\text{H}_2\text{O}$ to the reaction system appeared to have a marginal negative effect on the gypsum produced. A slight decrease in the mean particle size was evident and a deterioration in the filtration rate was also experienced in the presence of the impurity.

As mentioned previously, preparation of the impurity solutions in $\text{H}_2\text{SO}_4$ proved difficult at higher concentrations. Hence, solubility of some impurities in the slurry was investigated. This investigation involved dissolving 20g of $\text{MgSO}_4.7\text{H}_2\text{O}$ and 20g of $\text{FeSO}_4.7\text{H}_2\text{O}$ in
300mls of slurry. Malvern analysis on this slurry indicated a very significant change in the size distribution (the mean particle size result changed from 39µm to 78µm). From an overlay plot of the size distributions (see Figure 6.16), a shift in the distribution to the right is very evident.

![Figure 6.16: Malvern Overlay Plot](image)

This led to a further series of experiments of the same scale. These experiments involved the addition of 20g of an impurity to 300mls of slurry from the calcium citrate filter repulper (mean particle size = 41µm). The addition of MgSO₄·7H₂O resulted in an increase of mean particle size to 64µm while the addition of FeSO₄·7H₂O resulted in an increase in mean particle size to 55µm. The addition of both impurities together resulted in an increase in mean particle size to 77µm. The same impurities were added to gypsum slurry from the plants trim tank. The mean particle sizes were found to increase from 52µm initially, to 87µm, 95µm and 115µm respectively. When 5g and 10g of MgSO₄·7H₂O were added to the plant slurry (from calcium citrate filter repulper), the mean particle sizes were only found to increase to 43µm and 47µm respectively. The results of these experiments led to scale-up to the laboratory reactor size for further experimentation.
Objective: Investigate the effect of MgSO₄·7H₂O in the reaction mixture.

Procedure:
287g of MgSO₄·7H₂O was added to the calcium citrate filter repulper slurry in the reactor and a sample was taken. The H₂SO₄ (96% w/w) was added for reaction to gypsum and a second sample was taken. After a residence time of 1.5 hours, another sample was taken. An additional 234g of MgSO₄·7H₂O was then added to the gypsum slurry in the reactor and a final sample was taken. A second trial using MgSO₄·7H₂O was carried out by adding the 287g of impurity during the sulphuric acid addition.

Results:
The trial results are summarised in Table 6.23. Four samples were taken during trial 12.11 and these are numbered 1 to 4 in Table 6.23. The sample in trial 12.12 was taken after completion of the reaction to gypsum as well as after a 90 minute residence time period.

<table>
<thead>
<tr>
<th>Test</th>
<th>Filterability Test (ml/min.)</th>
<th>Test Temp. (°C)</th>
<th>D(v,0.5) (µm)</th>
<th>D(v,0.9) (µm)</th>
<th>D(v,0.1) (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control 12.11</td>
<td>----</td>
<td>----</td>
<td>52.16</td>
<td>104.50</td>
<td>12.80</td>
</tr>
<tr>
<td>Trial 12.11 - No. 1</td>
<td>----</td>
<td>----</td>
<td>60.07</td>
<td>133.55</td>
<td>13.13</td>
</tr>
<tr>
<td>Trial 12.11 - No. 2</td>
<td>857</td>
<td>69</td>
<td>83.47</td>
<td>175.90</td>
<td>25.20</td>
</tr>
<tr>
<td>Trial 12.11 - No. 3</td>
<td>----</td>
<td>----</td>
<td>87.86</td>
<td>185.96</td>
<td>27.83</td>
</tr>
<tr>
<td>Trial 12.11 - No. 4</td>
<td>588</td>
<td>65</td>
<td>100.36</td>
<td>219.09</td>
<td>37.13</td>
</tr>
<tr>
<td>Control 12.12</td>
<td>833</td>
<td>65</td>
<td>43.51</td>
<td>90.19</td>
<td>11.16</td>
</tr>
<tr>
<td>Trial 12.12</td>
<td>790</td>
<td>62</td>
<td>79.73</td>
<td>183.05</td>
<td>22.45</td>
</tr>
</tbody>
</table>

Table 6.23: MgSO₄·7H₂O Impurity Filterability and Malvern Results

Analysis and Discussion of Results:
The overall particle distributions were seen to shift significantly to the right in the presence of the impurity MgSO₄·7H₂O. Sample number 1 (trial 12.11) showed an increase in mean particle size from the initial calcium citrate slurry \(D(v,0.5) = 41.02\mu m\) to the slurry after addition of the impurity \(D(v,0.5) = 60.07\mu m\). The mean particle sizes of the laboratory gypsum slurry samples were also seen to be much improved on the control sample \(D(v,0.5) = 83.47\mu m, 87.86\mu m\) versus \(52.16\mu m\). This change in distribution is evident from the 90%
and 10% points in Table 6.23 and is also illustrated in the Malvern overlay plot given in Figure 6.17.

![Malvern Overlay Plot](image)

Figure 6.17: Malvern Overlay Plot

While 90% of the distribution lay under 104.5\,\mu m in the control sample, only 65% of the laboratory sample distribution lay under this size. The addition of more MgSO$_4$.7H$_2$O after the reaction was complete again illustrated an increase in mean particle size with a further shift in the distribution to the right. Despite the increased particle size results however, the filterability results did not improve. Also, microscopic analysis of the samples did not illustrate any significant changes in crystal appearance. However, after retaining the samples for 4 days, sample number 4 contained very visible needle-shaped crystals. These crystals were visible to the human eye and were approximately 6mm in length. Microscopic examination of these needles showed that the needles were actually agglomerates of small gypsum crystals.

The Malvern results from trial 12.12 also supported an improvement in particle size with 90% of the control distribution lying under 90.19\,\mu m while only approximately 57% of the laboratory sample distribution was smaller than 90\,\mu m. A Malvern overlay plot again illustrates this clearly (see Figure 6.18).
As for trial 12.11 however, the filterability test results did not improve even though the Malvern results did. The microscopic analysis supported the filtration test in that no significant crystal changes were evident. Analysis of the impurity content in the filtrates illustrated very high quantities of magnesium in the solution as was expected.

Conclusions:
Although the laboratory experiments with high impurity contents of MgSO₄·7H₂O, showed very significant changes in the particle size distributions, the slurry filtration rates did not change. This possibly suggests that although the overall particle distribution improved considerably, the filterability was inhibited by the presence of such large quantities of impurity. However, the fact that the particle size distribution improved once the impurity was added (even prior to the reaction) suggests that some of the impurity did not dissolve completely and the increase in particle size was actually due to particles of the impurity in the sample. The fact that no visible change in crystal size was evident from the microscopic analysis also suggests this theory. Atomic Absorption analysis proved that a significant quantity of the impurity remained in solution after filtration, therefore, on the plant scale, this impurity would be undesirably present in the citric acid solution.
Objective: Investigate the effect of FeSO₄·7H₂O in the reaction mixture.

Procedure:
287g of FeSO₄·7H₂O was added to the calcium citrate filter repulper slurry in the reactor and a sample was taken as done for trial 12.11. The H₂SO₄ (96% w/w) was added for reaction to gypsum and a second sample taken. An additional 257g of FeSO₄·7H₂O was then added to the gypsum slurry in the reactor and a sample taken. A final sample was taken after a residence time of 3 hours. A similar experiment was repeated to verify the results obtained.

Results:
The trial results are summarised in Table 6.24. Four samples were taken during trial 12.13 and three samples taken during trial 12.14. These are numbered 1 to 4 and 1 to 3 respectively in Table 6.24.

<table>
<thead>
<tr>
<th></th>
<th>Filterability Test (ml/min.)</th>
<th>Test Temp. (°C)</th>
<th>D(v,0.5) (µm)</th>
<th>D(v,0.9) (µm)</th>
<th>D(v,0.1) (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial Slurry</td>
<td>---</td>
<td>---</td>
<td>35.79</td>
<td>81.90</td>
<td>8.52</td>
</tr>
<tr>
<td>12.13</td>
<td>Control</td>
<td>750</td>
<td>42.28</td>
<td>87.15</td>
<td>11.14</td>
</tr>
<tr>
<td>Trial 12.13 - No.1</td>
<td>638</td>
<td>67</td>
<td>42.56</td>
<td>89.82</td>
<td>10.22</td>
</tr>
<tr>
<td>Trial 12.13 - No.2</td>
<td>638</td>
<td>67</td>
<td>77.66</td>
<td>178.95</td>
<td>23.03</td>
</tr>
<tr>
<td>Trial 12.13 - No.3</td>
<td>638</td>
<td>67</td>
<td>89.18</td>
<td>221.84</td>
<td>28.25</td>
</tr>
<tr>
<td>Trial 12.13 - No.4</td>
<td>---</td>
<td>---</td>
<td>61.76</td>
<td>167.82</td>
<td>15.99</td>
</tr>
<tr>
<td>Initial Slurry</td>
<td>---</td>
<td>---</td>
<td>35.31</td>
<td>79.88</td>
<td>8.50</td>
</tr>
<tr>
<td>12.14</td>
<td>Control</td>
<td>769</td>
<td>41.22</td>
<td>84.50</td>
<td>10.31</td>
</tr>
<tr>
<td>Trial 12.14 - No.1</td>
<td>682</td>
<td>68</td>
<td>82.12</td>
<td>179.78</td>
<td>25.98</td>
</tr>
<tr>
<td>Trial 12.14 - No.2</td>
<td>---</td>
<td>---</td>
<td>82.63</td>
<td>185.80</td>
<td>25.05</td>
</tr>
<tr>
<td>Trial 12.14 - No.3</td>
<td>682</td>
<td>65</td>
<td>89.72</td>
<td>222.59</td>
<td>28.18</td>
</tr>
</tbody>
</table>

Table 6.24: FeSO₄·7H₂O Impurity Filterability and Malvern Results

Analysis and Discussion of Results:
The difference in the Malvern particle size distribution between the initial calcium citrate slurry and the sample taken after the addition of impurity, was not as significant as previously experienced with the MgSO₄·7H₂O (increased from 35.79µm to 42.56µm as opposed to an increase from 41.02µm to 60.07µm for trial 12.11). The laboratory gypsum samples however, (i.e. after reaction with H₂SO₄) were found to increase from the control sample size distribution, as before. While 90% of the control distribution lay below 87.15µm, only approximately 57% of the test sample distribution lay below this value. The volume of
particles less than 10μm was found to decrease from about 10% to 5% of the distribution. When the slurry was sampled after a 3 hour residence time period, the slurry contained large visible globules and the slurry also seemed more viscous. The Malvern mean particle size had decreased to about 62μm at this stage and the volume of the distribution tail seemed to increase also from the previous two samples (see Figure 6.19).

![Malvern Overlay Plot](image)

Figure 6.19: Malvern Overlay Plot

The filterability tests suggested no improvement in the slurry filtration rates, the rates had even deteriorated slightly. Small gypsum crystals were still very evident from the microscopic analysis while the atomic absorption analysis suggested very large quantities of iron in the filtrates. The solids content in the filtrates were also analysed and an increase in the total solids content was found for sample number 3. The quantity of grey material (hemihydrate gypsum) did not change between the samples.

Similar results and trends were obtained from trial 12.14 with an increase in Malvern particle sizes while the filtration rates worsened. Analysis of the solids content again showed an increase in the brown layer for sample number 3. This extra quantity of solids was found to be crystals of FeSO₄ in the slurry. Microscopic inspection verified the presence of FeSO₄ crystals in the sample.
Conclusions:
The addition of FeSO$_4$.7H$_2$O to the reaction system produced results similar to those obtained from the addition of MgSO$_4$.7H$_2$O. Considerable changes in the particle size distributions were obtained while the slurry filtration rates were not altered. However, crystals of FeSO$_4$ were identified in these experiments which verifies that the change in the particle size distributions was due to crystals of the impurities as opposed to changes in the actual gypsum crystals. In practical terms, the quantities of impurities used for these experiments were unrealistic for the plant operation. However, if the gypsum crystal habit was altered by such an impurity, research into the identification of a substance similar in its habit modifying properties to the impurities tested, but effective in minute quantities could then be addressed.

Based on the investigation by Hasson et al., 1990 (see Chapter 2), the influence of Fe$_2$(SO$_4$)$_3$.xH$_2$O and Al$_2$(SO$_4$)$_3$.16H$_2$O on the gypsum formation were investigated. Therefore, some experimentation was carried out using these impurities in the laboratory. Initially, a series of beaker-scale experiments were carried out and these experiments were then scaled up to the laboratory reactor size. 5g, 10g and 15g of both impurities were added to 300mls of the slurry from the calcium citrate filter repulper. Each sample was analysed by the Malvern. The samples were also filtered and washed and the filter cake was then analysed by the Malvern also. The results obtained are shown in Table 6.25.

<table>
<thead>
<tr>
<th></th>
<th>Fe$_2$(SO$_4$)$_3$.7H$_2$O</th>
<th>Al$_2$(SO$_4$)$_3$.16H$_2$O</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>D(v,0.5)</td>
<td>D(v,0.9)</td>
</tr>
<tr>
<td><strong>Initial Slurry</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5g Impurity</td>
<td>37.61</td>
<td>90.33</td>
</tr>
<tr>
<td>Cake Sample</td>
<td>35.82</td>
<td>84.58</td>
</tr>
<tr>
<td>10g Impurity</td>
<td>42.90</td>
<td>96.50</td>
</tr>
<tr>
<td>Cake Sample</td>
<td>37.47</td>
<td>92.41</td>
</tr>
<tr>
<td>15g Impurity</td>
<td>50.33</td>
<td>108.34</td>
</tr>
<tr>
<td>Cake Sample</td>
<td>37.68</td>
<td>89.14</td>
</tr>
</tbody>
</table>

Table 6.25: Malvern Results from Beaker-Scale Experiments

The slurry changed to a green colour when the Fe$_2$(SO$_4$)$_3$.xH$_2$O was added, hence the addition of this impurity did not appear to be very practical. The Malvern results obtained from the initial experiments were not as significant as with the previous impurity trials but a laboratory reaction in the presence of these impurities was necessary to confirm this.
Objective: Investigate the effect of Fe\textsubscript{2}(SO\textsubscript{4})\textsubscript{3}.xH\textsubscript{2}O and Al\textsubscript{2}(SO\textsubscript{4})\textsubscript{3}.16H\textsubscript{2}O in the reaction mixture.

Procedure:
10g of Al\textsubscript{2}(SO\textsubscript{4})\textsubscript{3}.16H\textsubscript{2}O to 300mls of slurry was scaled up to 4.35 litres for the reactor. Therefore, 145g of Al\textsubscript{2}(SO\textsubscript{4})\textsubscript{3}.16H\textsubscript{2}O was added to the calcium citrate filter repulper slurry in the reactor and a sample was taken. The H\textsubscript{2}SO\textsubscript{4} (96% w/w) was added for reaction to gypsum and a second sample was taken. A similar experiment was carried out with Fe\textsubscript{2}(SO\textsubscript{4})\textsubscript{3}.xH\textsubscript{2}O. 145g of Al\textsubscript{2}(SO\textsubscript{4})\textsubscript{3}.16H\textsubscript{2}O was approximately 0.9 moles of Al\textsubscript{2}(SO\textsubscript{4})\textsubscript{3}.16H\textsubscript{2}O per litre of H\textsubscript{2}SO\textsubscript{4}. Therefore, to use the same concentration of Fe\textsubscript{2}(SO\textsubscript{4})\textsubscript{3}.xH\textsubscript{2}O required only 120g of the impurity. 120g of Fe\textsubscript{2}(SO\textsubscript{4})\textsubscript{3}.xH\textsubscript{2}O was added to the reactor and H\textsubscript{2}SO\textsubscript{4} was added for the reaction to gypsum. A sample was taken when the reaction was complete and another sample was taken after a residence time period of 3 hours. A third trial was carried out using a small quantity (0.1 mol. per litre of H\textsubscript{2}SO\textsubscript{4}) of Al\textsubscript{2}(SO\textsubscript{4})\textsubscript{3}.16H\textsubscript{2}O. This experiment was performed to check the literature theory of Hasson et al., 1990 which suggested that in the low impurity range, both Al\textsuperscript{3+} and Fe\textsuperscript{3+} acted to improve the gypsum filterability while in the high concentration range, the filterability was reduced. The trial samples were taken at the end of the reaction period and after 2.5 hours residence time.

Results:
The Malvern results of trials 12.15 and 12.16 are summarised in Table 6.26 and those of trial 12.17 are given in Table 6.27. The impurity concentrations given are expressed as moles of impurity per litre of H\textsubscript{2}SO\textsubscript{4}.

Table 6.26: Malvern Results for Trials 12.15 and 12.16

<table>
<thead>
<tr>
<th></th>
<th>0.9mol. Fe\textsubscript{2}(SO\textsubscript{4})\textsubscript{3}.7H\textsubscript{2}O</th>
<th>0.9 mol. Al\textsubscript{2}(SO\textsubscript{4})\textsubscript{3}.16H\textsubscript{2}O</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$D(v,0.5)$</td>
<td>$D(v,0.9)$</td>
</tr>
<tr>
<td>Initial Slurry</td>
<td>42.50</td>
<td>86.23</td>
</tr>
<tr>
<td>Control</td>
<td>41.14</td>
<td>78.80</td>
</tr>
<tr>
<td>Test Sample 1</td>
<td>44.16</td>
<td>90.14</td>
</tr>
<tr>
<td>Test Sample 2</td>
<td>45.62</td>
<td>86.44</td>
</tr>
<tr>
<td></td>
<td>0.1 mol. Al₂(SO₄)₃·16H₂O</td>
<td></td>
</tr>
<tr>
<td>------------------</td>
<td>--------------------------</td>
<td>------------</td>
</tr>
<tr>
<td></td>
<td>D(v,0.5)</td>
<td>D(v,0.9)</td>
</tr>
<tr>
<td>Initial Slurry</td>
<td>38.07</td>
<td>87.40</td>
</tr>
<tr>
<td>Control</td>
<td>42.37</td>
<td>92.01</td>
</tr>
<tr>
<td>Test Sample 1</td>
<td>42.42</td>
<td>88.75</td>
</tr>
<tr>
<td>Test Sample 2</td>
<td>43.14</td>
<td>88.19</td>
</tr>
</tbody>
</table>

Table 6.27: Malvern Results for Trial 12.17

**Filterability Test**

Control 12.15/12.16: 1154 ml/min. @ 70°C
Trial 12.15: 1200 ml/min. @ 67°C
Trial 12.16: 1154 ml/min. @ 67°C
Control 12.17: 732 ml/min. @ 66°C
Trial 12.17: 1000 ml/min. @ 67°C

**Analysis and Discussion of Results:**

The Malvern results for all the trials did not change significantly from the control to the test samples. The filterability results for trials 12.15 and 12.16 were almost the same for both the control and test samples. In trial 12.17, the test filterability result appeared better than the control. However, the control filtration rate appeared low in this case and the test result was not improved considerably. The residence time of 3 hours in trial 12.16 or the 2.5 hour period in trial 12.17 had no effect on the distributions. The microscopic analysis did not indicate any changes in the crystal appearance. The slurry turned green in colour in the presence of Fe₂(SO₄)₃·xH₂O while no colour change was experienced with the Al₂(SO₄)₃·16H₂O impurity.

**Conclusions:**

The main conclusion drawn from these trials was that the changes in the Malvern results were not nearly as significant as the previous experiments performed with impurities. Overall, the gypsum filtration rate was not improved greatly and no changes in the gypsum crystal habit were experienced. Although these impurities had a positive influence on the gypsum produced in the phosphoric acid process (Hasson et al, 1990), they do not appear to have the same effect on the gypsum produced in the citric acid process.
6.5.13 Investigation 13: Reaction of $\text{H}_2\text{SO}_4$ (96% w/w) with Pure Calcium Citrate Formed from Pure Reagents

6.5.13.1 Introduction

The experiments described in Section 6.5.12 investigated the effects of additional quantities of various impurities on the gypsum crystal formation. In order to investigate the effects (if any) of the impurities already in the reaction system, gypsum was formed from pure reagents and a comparison was made between the pure gypsum formed in the laboratory and the impure gypsum being formed in the plant. [In order to respect ADM's confidentiality, the general term 'reactant' is used instead of the actual material in the following experiment descriptions]

Objective: Compare the gypsum formed from pure reactants with that being produced in the plant.

Procedure:

Pure reactants were reacted with a 12% w/w pure citric acid solution to form pure calcium citrate. A reaction mixture of approximately 25% solids content was prepared. 250g of reactant was added very slowly to the citric acid solution. Samples were taken at intervals during the reactant addition for analysis of the solids content. When approximately 25% solids was achieved, the reaction mixture was allowed to stir for 4 hours. A sample was taken after 1 hour and also after 4 hours. A calcium citrate assay was performed on the 4 hour sample. The entire reactor contents were then filtered and washed and the calcium citrate cake was retained. This procedure was repeated twice in order to form enough calcium citrate for decomposition to gypsum with sulphuric acid. When enough calcium citrate cake had been obtained, water was added to slurry the cake and to provide an appropriate operating level in the reactor (approximately 3 litres). The specific gravity of this mixture was measured (S.G. = 1.04) and was then decomposed with 96% w/w $\text{H}_2\text{SO}_4$ to produce pure gypsum. A similar reaction was carried out with calcium citrate cake from the plant. The cake was slurried in water to give a volume of about 3 litres and a specific gravity of 1.04. Gypsum was then produced as a result of decomposition with $\text{H}_2\text{SO}_4$ (96% w/w). Filterability tests and solids analysis were carried
out on the samples. The end-point of the filterability tests however were difficult to determine. Due to the low slurry specific gravities, the filtrations took place very rapidly. Therefore the results obtained may not be entirely accurate and cannot be compared to the usual slurry filtration rates.

**Results:**

<table>
<thead>
<tr>
<th></th>
<th>Pure Reactants</th>
<th>Plant Reactants</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>D(v,0.5)</td>
<td>D(v,0.9)</td>
</tr>
<tr>
<td>Calc. Citrate Cake</td>
<td>26.53</td>
<td>59.99</td>
</tr>
<tr>
<td>Gypsum</td>
<td>76.57</td>
<td>160.85</td>
</tr>
</tbody>
</table>

Table 6.28: Malvern Results

**Solids Results:**

- Pure Reactants: 0.15% Total Solids with < 0.05% Hemihydrate Gypsum
- Plant Reactants: 0.20% Total Solids with ~ 0.07% Hemihydrate Gypsum

**Analysis and Discussion of Results:**

The gypsum crystals formed from the pure reactants were found to be of better quality than the crystals normally produced. Larger, more uniform crystals were evident from the microscopic analysis (see Figure 6.20). In comparison, the crystals formed from the plant materials were small and agglomeration of the particles was also evident. The Malvern results also supported this with a mean particle size of 76.57µm for the pure gypsum as opposed to a size of 63.61µm obtained from the plant materials. The analysis of the solids content in the filtrates suggested that a smaller amount was achieved with the pure reactants and it also appeared to contain less hemihydrate material.
Conclusion:
Overall, the gypsum obtained from the pure reactants appeared to be of better quality than the crystals normally formed. When the pure calcium citrate was being prepared from the pure reactants and pure citric acid solution, the mixture tended to become very viscous and even paste-like. Therefore, the quantity of reactant that could be added to the citric acid solution was quite small if the mixture was to be maintained in suspension. Therefore, to obtain enough calcium citrate to achieve the plant specific gravities would involve repeating the experiment several times. Due to time constraints, this did not seem a feasible option. Hence, it was not possible to measure the gypsum filtration rate at the plant specific gravity. However, it is likely that the filtration rates would have been improved over the existing rates due to the physical improvement in crystal quality as well as the increase in Malvern particle size.

Objective:
Using reactants from the plant, react with 12% w/w citric acid solution and compare the resulting calcium citrate with that produced from pure reactants.

Procedure:
Reactant was taken from the plant and the particle size distribution was measured. 350g of the material was then added to 12% w/w citric acid solution and allowed to react for approximately 28 hours. 250g of the material was added initially (250g of the pure reactant was used) but the specific gravity of the slurry was very low in comparison to that obtained from the pure reactant. This was due to the fact that the plant reactant contained approximately 50% moisture while the pure reactant was dry. Therefore an additional 100g of the plant reactant was added. The particle size of a sample taken after 28 hours was measured and analysed using the microscope. The results were compared with the calcium citrate obtained from pure reactants as described in the previous experiment.
Results:

<table>
<thead>
<tr>
<th>Mean Particle Sizes</th>
<th>Plant</th>
<th>Pure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reactant</td>
<td>63.87μm</td>
<td></td>
</tr>
<tr>
<td>Calcium Citrate Slurry</td>
<td>69.97μm</td>
<td>43.36μm</td>
</tr>
<tr>
<td>Calcium Citrate Cake</td>
<td>23.77μm</td>
<td>26.53μm</td>
</tr>
</tbody>
</table>

Analysis and Discussion of Results:

From the microscopic analysis, a significant quantity of unreacted material was evident in the 28 hour sample. This was also supported by the Malvern result which illustrated a particle size distribution containing 2 peaks (see Appendix F). These peaks represented both unreacted material and calcium citrate particles. The mean particle size obtained (69.97μm) also seemed high for calcium citrate alone. After filtering and washing the sample, the distribution appeared to be close in shape to the ‘expected’ distribution and the mean particle size was also similar to that of the calcium citrate normally obtained from the plant. The calcium citrate appeared to be less uniform in shape to the calcium citrate obtained from the pure reactant. The fact that the reactant material did not completely convert to calcium citrate even though the reaction time was 28 hours, suggested that the ratio of reactant to citric acid was too high.

Conclusion:

Even though the reactant material had not fully converted to calcium citrate at the end of the 28 hours, the calcium citrate that was evident appeared to be less uniform in shape to that obtained from the pure reactants. However, the mean particle size of the calcium citrate cake obtained after filtration and washing, was close to that obtained from the pure reactants as well as the plant calcium citrate.

Objective: React pure calcium citrate slurry with 96% w/w H₂SO₄ to form gypsum.

Procedure:

250g of pure reactant was added to 12% w/w pure citric acid solution and allowed to react to form calcium citrate for approximately 17 hours. The H₂SO₄ was then added to the calcium citrate slurry (as opposed to filtering and washing the slurry and then reacting the acid with the
cake). A sample was taken at the end of the acid addition period and also after 5.5 hours residence time. The results were compared to those from the procedure described in Section 6.5.6.

**Results:**

<table>
<thead>
<tr>
<th>Mean Particle Sizes:</th>
<th>Plant</th>
<th>Pure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcium Citrate Slurry</td>
<td>55.33(\mu m)</td>
<td>56.75(\mu m)</td>
</tr>
<tr>
<td>Gypsum Slurry</td>
<td>62.53(\mu m)</td>
<td>78.00(\mu m)</td>
</tr>
<tr>
<td>Gypsum Slurry (+ Res. Time)</td>
<td></td>
<td>83.13(\mu m)</td>
</tr>
</tbody>
</table>

**Analysis and Discussion of Results:**

The mean particle size of the pure gypsum was found to be higher than that obtained from the plant calcium citrate slurry. The microscopic analysis illustrated that the crystals formed from the plant slurry were uniform, parallelogram shaped, plate-like crystals (see Figures 6.21 and 6.22).

Figure 6.21: Gypsum from Plant Slurry

Figure 6.22: Gypsum from Pure Slurry
and 6.22). The crystals from the pure calcium citrate slurry appeared to be less uniform and of a longer rectangular shape. The difference in shape (i.e. the larger longitudinal axis for the pure crystals) explains the difference in Malvern results between the two crystal types.

Conclusion:
Overall, the gypsum crystals obtained from the decomposition of both the pure and impure calcium citrate slurries were found to be of better quality than those normally obtained on the plant. However, the filtration rates of these slurries could not be compared to the plant rates due to the lower specific gravities as a result of the reaction with the calcium citrate slurry, as opposed to the normal decomposition of the calcium citrate cake slurried with gypsum slurry recycle from the strike tank (see Section 3.2.8).

6.5.14 Miscellaneous Laboratory Investigations

EXPERIMENT 14.1

Objective:
Remove the fine solids from the gypsum slurry and compare the Malvern result to that of the actual slurry.

Procedure:
Samples from the plant trim tank were filtered in the laboratory. The cake was retained while the filtrate was spun in cuvettes in a centrifuge. The filtrate was poured from the cuvettes while the fine solids remained at the end of the cuvettes. The filtrate was used to re-slurry the cake.

Results:
The Malvern analysis on the initial trim tank sample gave a mean particle size of 41.18μm. 10% of this distribution lay above 81.56μm and 10% below 11.75μm. The sample without the fine solids gave a mean particle size of 34.67μm with 10% of the distribution lying above 73.79μm and 10% lying below 9.72μm.
Analysis:
An overlay plot of the two distributions is given in Fig. 6.23 below.

Discussion:
From Figure 6.23, it is evident that the distribution of the test sample shifted slightly to the left of the control sample distribution. The tails of the two distributions extended to exactly the same point while it was expected that the tail of the sample without the fine material would be shorter. Examination of the Histogram reports (Appendix G) suggested a very slight decrease in the percentage of particles in the tail of the test sample. A repeat experiment produced the same trend with a less significant shift in the distribution to the left.

Conclusion:
From this experiment, it appeared that the absence of fine particles had no significant effect on the particle size distribution. This suggested that the fine particles of hemihydrate gypsum in the presence of a dihydrate gypsum sample are not significant enough to be recognised by the Malvern instrument. However, as illustrated in Section 6.5.4, significant quantities of hemihydrate gypsum were recognisable by the Malvern.
EXPERIMENT 14.2

Objective:
Compare the mean particle size of calcium citrate filtered in the laboratory to that filtered in the plant.

Procedure:
A sample of calcium citrate slurry was filtered in the laboratory. The mean particle size of the resulting cake was measured and compared to the cake obtained in the plant.

Analysis:
The Malvern results indicated no change in mean particle size between the plant and laboratory filtered calcium citrate. This eliminated the possibility that the pump transferring the slurry to the plant filters was breaking up the crystals. The decrease in mean particle size from the calcium citrate slurry to the corresponding cake was explained by the presence of calcium citrate grit in the slurry which settled out before reaching the filter both in the laboratory and plant scale.

Conclusion:
During the database development (Section 3.3.3), it was thought that the pump transferring the calcium citrate slurry to the filters was causing crystal damage. The experiment described above however, verified that the transfer pump was not the cause of the significant decrease in mean particle size between the calcium citrate slurry and filter cake samples. It can now be concluded that the particle size decrease is caused by the presence of large grit particles in the slurry which settle out before reaching the filters. Therefore, these particles are not present in the cake samples.
6.5 Southport Sample Analysis

The ADM plant at Southport claim to obtain good quality dihydrate gypsum without the formation of hemihydrate. In an effort to identify the differences in quality and size of the gypsum crystals between those formed at Southport and Ringaskiddy, a series of samples were requested from the Southport plant.

A selection of primary and secondary sour cake samples (corresponding to cake samples obtained from filtering the strike and trim tank samples at Ringaskiddy) were analysed using the Malvern particle sizer. The mean particle sizes of the primary samples were found to lie between 40 and 73μm. The mean particle sizes of the secondary samples were in the range of 62 - 78μm. From the Malvern analysis, on average, 8% of the particles were smaller than 10μm and 26% of the distribution had particles larger than 102μm. A comparison of the particle distributions of a set of primary and secondary sour samples is illustrated in Figure 6.24.

![Figure 6.24: Comparison of Southport’s Primary and Secondary Samples](image)

Overall, the mean particle sizes obtained from the Southport samples were better than those produced at Ringaskiddy, especially when the vortex mixer is on line.

Microscopic examination of the cake samples revealed a majority of rectangular-shaped, plate-like crystals. As supported by the Malvern analysis, the range of crystal sizes in a particular
sample still appeared quite large. However, the crystal appearances were of better quality than those of the Ringaskiddy samples. Visual evidence of the improved crystals can be seen in Figures 6.25(a) and (b).

The filtrate samples received appeared to have been laboratory filtered due to the absence of any significant solid material in the filtrates. When some cake sample was re-slurried with the corresponding filtrate and then filtered using a 1746 PES filter cloth [as on the gypsum pannevis filter], some solid material was evident in the filtrate.

Overall, the crystals appeared to be of good quality with relatively uniform shape. However, due to the large size range of crystals, the filterability is likely to be somewhat inhibited from that expected from the larger particles. It was not possible to achieve conclusive filterability results as the samples received had already been separated.
Chapter Seven

Plant Modification Options
Chapter Seven - Plant Modification Options

7.1 Introduction
This chapter outlines the importance of mixing on the control of chemical reactions and describes how the development of fluidic technology has improved the control of chemical reactions. However, due to the problems of reduced gypsum particle size at ADM, as a result of vortex mixing, options for an alternative sulphuric acid dispersion system in the gypsum reaction tank were investigated. An enquiry was made to ADM, Southport about the gypsum reaction set-up in Southport. A description of the gypsum reaction tanks, the agitation mechanism and the sulphuric acid dispersion system was received. Interaction with agitation and mixing experts also provided some suggestions for plant modifications which would facilitate improved sulphuric acid dispersion within the reaction tank.

7.2 Chemical Reaction Control Using Mixing Technology
A key step in the control of many chemical reactions within the process industry is control over the initial contacting of the reagents. The dissipation of mixing energy in a variety of stirred tank geometries is widely recognised as having a direct bearing on the outcome of many chemical reactions. A wide range of energy dissipations can exist within a stirred tank reactor. The value of the energy dissipation is a function of the distance from the tip of the agitator blade. Typically, there is a difference of two orders of magnitude between the local energy dissipation rates adjacent to the agitator tip and the dissipation at the perimeter of the vessel. These variations in mixing intensity have an effect on the micromixing performance of the vessel. In critical areas of the vessel, high concentration gradients can exist and these are sometimes regions of poor micromixing.

When the final product of a reaction is a solid, the degree of supersaturation has a profound effect on the rate of homogeneous nucleation of the crystalline phase (exponential relationship between supersaturation and nucleation). The number of nuclei produced ultimately determines the mean size of the population. In a stirred tank reactor with poor micromixing, the degree of supersaturation is high at the feed point of the precipitants. Hence the local nucleation rate will be large and the growth rate will be variable throughout
the volume of the vessel. The likely effect of such reaction conditions is a population with a small mean size and a wide spread of size.

It may appear that by increasing the agitator power, all regions of the tank could be subject to a greater level of mixing and therefore local variations in reactant concentrations would be minimised. However, in many cases, solid reaction products are shear-sensitive and excessive mixing may produce product breakage. In the case of crystallization, secondary nucleation may occur, again resulting in a population with a low mean size and a wide spread of size. Therefore, when product size distribution is an important consideration, there is usually an optimum degree of mixing required to achieve the desired product quality and consistency. This optimum may exist over a narrow range of mixing energy dissipations. Therefore, the ideal mixing intensity may be extremely difficult to achieve throughout the vessel volume, therefore lowering the product quality and reducing the overall consistency.

The introduction of fluidic mixing technology provided an attractive alternative with the ability to achieve uniform mixing and overcome the problems of poor micromixing in stirred tank reactors. Fluidic technology employs hydrodynamic forces which exist within the process fluids themselves to achieve mixing and is based on the understanding of vortex flow. The requirements are an appropriate source of pressure energy and the correct enclosure geometry.

In principle, fluidic technology works by the introduction of reagent streams tangentially into a mixing chamber (see Figure 3.2). Differences in inlet velocity promote rapid momentum transfer at the outer perimeter of the chamber. The partially mixed stream then migrates towards a central exit port, increasing the tangential velocity component by the conservation of angular momentum. Effective micromixing is achieved as eddy diffusion can reduce concentration gradients to desired levels before exit from the contacting chamber. The technology can be used to control mixing operations with reactor residence times from milliseconds to hours, using a range of different devices.

The vortex mixer can be used for the control of rapid chemical reactions. Within this mixer, a number of inlet streams can intermix in a tightly-wound vortex spiral. The mixing chamber
is completely open and requires no packing. Mixing times of approximately 5 milliseconds can be achieved, allowing mixing to take place during the induction period of the reaction.

7.3 Plant Modification Options Research

7.3.1 Introduction

Having undertaken a considerable amount of experimental work in the area of gypsum crystallization, it appears that once the gypsum crystals have been formed, no improvement in the crystal size or filtration rate is possible, i.e. no significant crystal modification is possible once the conversion from calcium citrate to gypsum has taken place. Therefore, while the vortex mixer is on line, the gypsum crystal size cannot be increased.

Some initial research was carried out on the plant modification options available, with a view to bypassing the vortex mixer and improving the sulphuric acid dispersion system in the strike tank, i.e. eliminating the formation of "hot-spots". The main sources of this research were an enquiry to ADM, Southport and interaction with expert agitator and mixer vendors such as APV, Chemineer and Lightnin'.

7.3.2 Southport's Sour Reaction Set-Up

The following is the response of an enquiry to Mr. Jim Attack (ADM, Southport) on the sour reaction set-up in Southport:

Two primary sour tanks (T-419-1 and T-419-2) and one secondary sour tank (T-420) exist with tank capacities of approximately 16,000 gallons each. T-419-1 and T-419-2 are spares for each other. T-419-2 is normally operated with T-419-1 on standby. The standby primary tank T-419-1 and the secondary tank have the same set-up and conditions. The impellers used are A310 with speeds of 84 rpm in the primary tank and 68 rpm in the secondary. The impeller diameters are 72 inches and 70 inches in the primary and secondary tanks respectively with the impellers 36 inches and 35 inches off the tank bottom.

8 sulphuric acid dip tubes are used in the primary tank and 4 sulphuric acid dip tubes are used in the secondary tank. The dip tubes are equally spaced with a 36 inch radius from the
agitator centreline. The dip tubes extend down into the tank to within 12 inches above the agitator impeller. Turnovers per min. of 4.37 and 3.85 are achieved in the primary and secondary tanks.

7.3.3 Modification Suggestions From APV

The existing agitation arrangement in the strike tank which provides 4 turnovers per min. is not enough to achieve the mixing necessary to disperse the sulphuric acid rapidly throughout the strike tank. The following suggestions were made by APV:

1. In order to increase the number of turnovers per min., a bigger agitator would be necessary. However, the scope of agitator size increase is limited due to the size of the actual strike tank. Therefore, a bigger agitator would also require a larger vessel.

2. The use of two agitators in the current strike tank would provide slightly better agitation.

3. Separate off a small section of the strike tank which would incorporate a small agitator. Add the sulphuric acid to the slurry in this small section for the actual reaction to gypsum. Use a weir-type arrangement to overflow the mixed slurry (i.e. gypsum) into the main reaction vessel and use the existing agitator to keep the solids in suspension.

4. Use a series of dip tubes to add the acid to the existing tank. Position the tubes behind the tank baffles to eliminate any mechanical stability problems. Use 90° bends at the end of the tubes and extend the discharge points just under the agitator blade tips where the mixing intensity would be highest.

7.3.4 Modification Suggestion From Chemineer

Chemineer suggested the use of a Kenics Static mixer (see Appendix H) to meet the mixing requirements for the gypsum reaction. This static mixer would premix the slurry and acid before it is introduced into the strike tank. Mixing to homogeneity can be achieved in fractions of a second in a Kenics mixer.

The Kenics static mixer has a more gentle action than a vortex mixer and because the mixer would be used as a premix device, the use of only two elements could be employed. This would minimise the risk of gypsum particle size reduction.
7.3.5 Modification Suggestion From Lightnin’ Mixers

Lightnin’ recommended the use of a Lightnin A310 high efficiency impeller (see Appendix I) to provide the required rapid blending with low shear to prevent damage to the crystals.

7.4 General Comments

1. The current agitator in the strike tank provides a turnover of 4 per minute which is similar to the turnover used in Southport’s reaction tanks. However, because the sulphuric acid discharge is in one spot only, the turnover is not sufficient to provide the necessary mixing, hence the formation of “hot-spots”.

2. The existing 1” acid dip pipe extends only slightly below the liquid surface which means it is not near the most effective mixing point.

3. From the laboratory experiments performed, it was possible to achieve the same low quantity of hemihydrate in the laboratory as with the vortex mixer on-line. This leads to the conclusion that with an adequate dispersion system within the strike tank, the same effects could be obtained in the plant scale, i.e. maintain the low percentage of hemihydrate.

4. Suggestions 3 and 4 by APV do not involve changing the existing agitation mechanism. Therefore, these modifications could be made with the option of returning to the old mechanism if required. Since the use of multiple acid discharge points within the tank has been successful for Southport, option 4 seems especially promising.

5. Incorporation of the Kenics static mixer still presents a “chance” that the particle size may be reduced. Therefore, in view of the objective to increase the particle size, after initial enquiries, this does not seem a very promising modification.

6. If installation of a new agitator(s) is required, the A310 model seems to be the most favourable. This design is used by Southport and the same design was also recommended by APV.
Chapter Eight

Conclusions and Recommendations
8.1 Conclusions

The purpose of this research project was to characterise and optimise the gypsum crystallization step of the citric acid production facility at ADM Ringaskiddy. The project sought to retain the advantages conferred by the vortex mixer but subsequently grow larger gypsum crystals in order to at least reclaim the design gypsum filtration capacity. The main objectives of the project were to:

- Develop a detailed technical understanding of the factors which influence the nucleation of gypsum crystals and the resultant filterability of gypsum.
- Characterise the existing gypsum crystallization reaction process.
- Define the existing gypsum production limitations.
- Design and construct a pilot laboratory experimental rig to simulate plant conditions and facilitate investigating trials.
- Evaluate options to overcome the current gypsum production limitations.

The literature search carried out at the initial stages of the project developed a thorough understanding of the general crystallization process and associated terminology. A significant amount of information was also obtained from specific literature in relation to gypsum crystallization. Much of the literature reviewed, provided a useful background knowledge for the entire project development. Some of the literature was also used as a basis in the development of the pilot laboratory experimental programme.

The development of the comprehensive database enhanced the technical understanding of the existing gypsum production process at Ringaskiddy, identified the variation of crystal shape and size distribution along the formation path and provided an improved knowledge of the production limitation issues to be addressed throughout the project.

The pilot laboratory experimental rig was successfully designed and constructed to simulate the plant conditions and also facilitated the performance of an intensive period of experimental trials. A thorough hazard and safety assessment of the rig and the general laboratory environment, prior to any experimentation, ensured that all experiments were carried out in a safe manner.
From the experiments carried out during the project, the following conclusions can be made:

The optimum gypsum reaction temperature is 80°C which is the approximate temperature at which the plant gypsum reaction normally takes place.

The pump transferring the calcium citrate slurry to the calcium citrate filters is not the cause of the significant decrease in mean particle size between the calcium citrate slurry and filter cake samples. The particle size decrease appears to be caused by the presence of large grit particles in the slurry which settle out before reaching the filters. Therefore, these particles are not present in the cake samples.

The addition of sulphuric acid to the gypsum reaction vessel, even when the calcium citrate conversion is complete, tends to increase the gypsum mean particle size. The addition of significant quantities of excess acid is obviously not a practical consideration for the plant, but it is interesting to note that the continual increase in mean particle size after the calcium citrate was fully converted, was found to be a result of the additional acid being added and not (as originally speculated) due to residence time in the reactor.

Residence time alone does not influence the gypsum crystal size. Therefore, extending the gypsum slurry capacity in the plant to increase the residence time of the crystals would not be of benefit to the gypsum crystal size.

The use of lower concentrations of sulphuric acid resulted in a slight improvement in mean particle size and filterability results. Unfortunately, these improvements were not significant enough to warrant further investigation.

Microcrystalline hemihydrate material was successfully formed by using high $\text{H}_2\text{SO}_4$ flowrates and low agitation speeds to create ‘hot-spots’ within the reactor. An excess quantity of acid was also used to cause ‘product burning’. The combination of these conditions to produce the microcrystalline material verified the required conditions for this production. The filtration of the slurry proved that the material was capable of getting through the filter cloth which, in the plant scale, would then be undesirably present in the refining end. A high possibility of filter cloth blinding also existed which would be detrimental to the gypsum filtration step. These trials demonstrated the conditions which should be avoided in the plant at all times in an effort
to eliminate the production of hemihydrate gypsum. The resulting effects of the undesirable conditions were also clearly illustrated.

The absence of fine particles from the gypsum slurry had no significant effect on the particle size distribution. This suggested that the fine particles of hemihydrate gypsum in the presence of a dihydrate gypsum sample are not significant enough to be recognised by the Malvern instrument. However, as illustrated in Section 6.4.4, significant quantities of hemihydrate gypsum were recognisable by the Malvern.

The reaction of $\text{H}_2\text{SO}_4$ with calcium citrate cake produced low quality crystals with poor washing and filtration characteristics. The physical nature of the slurry also suggested handling difficulties which, in the large scale would pose a problem. This trial emphasised the necessity of the reaction to take place in a slurry form, with the $\text{H}_2\text{SO}_4$ added below the slurry surface.

Trials with calcium citrate slurry suggested significant improvements in the gypsum crystals and hence improved filtration rates. Plate-like parallelogram-shaped crystals of gypsum were formed and the filterability result appeared to be much improved on the control samples. The reaction of calcium citrate to gypsum in the presence of the citric acid mother liquor, gave promising initial results with a view to the development of a possible solution to the plant gypsum filtration problems.

The presence in the reaction, of citric acid mother liquor from the pannevis filtrate, did not have the same improved effect on the gypsum crystals as the calcium citrate slurry reaction. This suggested that some impurity present in the citric acid liquor prior to the calcium citrate filtration stage (but not present in the liquor remaining after the pannevis filtration), had a positive effect on the crystals.

Reactions using water to slurry the calcium citrate cake produced smaller, needle-shaped crystals.

Microscopic analysis of the initial trials using filtrate from the calcium citrate filtration step to slurry the calcium citrate cake, clearly illustrated that much better crystals were achieved. This result agreed with those obtained using calcium citrate slurry. The Malvern analysis also supported the microscopic evidence of improved crystal size with mean particle sizes of
approximately double the control values achieved. These trials, combined with the trial using filtrate from the pannevis filtration step, suggested that some impurity removed at the calcium citrate filtration stage, had a beneficial effect on the gypsum crystals. Continuing trials rejected this theory while suggesting that the improved crystals obtained previously were as a result of a much lower slurry specific gravity. The experiments performed with slurries of high specific gravity showed no improvement in crystal size or appearance.

Preliminary experiments in the presence of Sodium and Potassium Citrate impurities suggested a positive influence on the gypsum crystals. Although the Malvern results were found to be relatively normal with the Potassium Citrate alone, when analysed microscopically, the crystals appeared much better than the usual gypsum crystals. The difference in Malvern results between this and the other experiments was explained by the actual shape of the crystals. The longitudinal axis appeared longer in the presence of Sodium Citrate which explained the larger Malvern results. The volume of particles in the tail of the distribution appeared smaller in the experiment with Sodium Citrate alone (only 10% of particles smaller than 26μm). This theory was eliminated however by further experimentation. It was found that with a high dilution factor, improvements in crystal size and overall crystal appearance could be obtained, with or without the Sodium or Potassium Citrate.

Since the citric acid broth from the fermentation stage of the process contains both soluble and insoluble impurities, in order to determine the influence (if any) of these impurities on the gypsum formation step, additional quantities of the cationic impurities were added to the reaction mixture.

The addition of K₂SO₄ did not influence the gypsum crystals. The mean particle sizes remained practically unchanged and any fluctuations in the filtration rates were not significant. Since the potassium remained in the citric acid solution after the conversion to gypsum had taken place, increase of the impurity concentration above the concentrations tested, did not seem practical.

The addition of Na₂SO₄.10H₂O to the reaction system appeared to have a marginal negative effect on the gypsum produced. A slight decrease in the mean particle size was evident and a deterioration in the filtration rate was also experienced in the presence of the impurity.
Although the laboratory experiments with high impurity contents of MgSO$_4$.7H$_2$O showed very significant changes in the particle size distributions, the slurry filtration rates did not change. Initial speculation suggested that although the overall particle distribution improved considerably, the filterability was inhibited by the presence of such large quantities of impurity. However, the fact that the particle size distribution improved once the impurity was added (even prior to the reaction) suggested that some of the impurity did not dissolve completely and the increase in particle size was actually due to particles of the impurity in the sample. The fact that no visible change in crystal size was evident from the microscopic analysis also supported this theory.

The addition of FeSO$_4$.7H$_2$O to the reaction system produced results similar to those obtained from the addition of MgSO$_4$.7H$_2$O. Considerable changes in the particle size distributions were obtained while the slurry filtration rates were not altered. However, crystals of FeSO$_4$ were identified in these experiments which verified that the change in the particle size distributions was due to crystals of the impurities as opposed to changes in the actual gypsum crystals.

In practical terms, the quantities of impurities used for these experiments were unrealistic for the plant operation. Atomic Absorption analysis also proved that a significant quantity of the impurity remained in solution after filtration, therefore, on the plant scale, the impurities would be undesirably present in the citric acid solution. However, it was hoped that if the gypsum crystal habit was altered by such an impurity, research into the identification of a substance similar in its habit modifying properties to the impurities tested, but effective in minute quantities could then be addressed.

Although Fe$_2$(SO$_4$)$_3$.xH$_2$O and Al$_2$(SO$_4$)$_3$.16H$_2$O impurities had a positive influence on the gypsum produced in the phosphoric acid process (Hasson et al, 1990), they were not found to have the same effect on the gypsum produced in the citric acid process.

The gypsum obtained from pure reactants appeared to be of better quality than the crystals normally formed. [The calcium citrate formed from the plant reactants appeared to be less uniform in shape to that obtained from the pure reactants]. However, the mean particle size of the calcium citrate cake obtained after filtration and washing, was close to that obtained from
the pure reactants as well as from the plant calcium citrate. Overall, the gypsum crystals obtained from the decomposition of both the pure and impure calcium citrate slurries were found to be of better quality than those normally obtained on the plant. The filtration rates of these slurries could not be compared to the plant rates due to the lower specific gravities resulting from the reaction with calcium citrate slurry, as opposed to the normal decomposition of calcium citrate cake slurried with gypsum slurry recycle from the strike tank.

On completion of the intensive experimentation period performed in this study, it can be concluded that it is not possible to improve the gypsum crystal size and filtration rate while the vortex mixer is on-line. Experiments carried out on the gypsum slurry downstream of the vortex mixer demonstrated that once the crystals have been formed, the crystal size cannot be increased by any chemical means. At this stage, as small crystals have been formed, their filtration rate has been decreased. The reactions carried out using calcium citrate and sulphuric acid proved that the most significant improvement in gypsum crystal size was obtained when the reaction was performed at a low specific gravity. This reaction method would be undesirable in the plant however due to the increased evaporative loads on the downstream evaporators. The addition of impurities to act as habit modifiers did not influence the crystals as was found by researchers in the phosphoric acid industry.

From the experiments performed, it was possible to achieve the same low level of microcrystalline gypsum in the laboratory as with the vortex mixer on-line. This led to the conclusion that with an adequate sulphuric acid dispersion system within the main gypsum reaction vessel, the same effect should be achievable in the plant scale (i.e. maintain the low level of microcrystalline gypsum).

8.2 Recommendations

On completion of this project, it appears that the most beneficial modification to the gypsum crystallization step of the citric acid production process, would be the removal of the vortex mixer and replace it with an improved sulphuric acid dispersion system within the reaction vessel. Plant trials have verified that the gypsum crystal size and filtration rates are much
improved when the vortex mixer is off-line. Hence, if the level of microcrystalline gypsum can be reduced without using the vortex mixer, the current citric acid production limitations as a result of the gypsum filtration rate, should be essentially eliminated. It is recommended that any further work to be carried out in this area should concentrate on the development of a new sulphuric acid dispersion system with a view to reducing the quantity of microcrystalline gypsum being formed.

Some of the options available for an alternative sulphuric acid dispersion system were investigated briefly at the close of the project. This preliminary research resulted in the following possibilities for plant modifications:

1. Extend the sulphuric acid dip-pipe to the most effective mixing point of the vessel.
2. Increase the number of turnovers per minute in the vessel. This would require a larger agitator. Since the scope of agitator size increase is limited due to the size of the existing reaction vessel, a larger agitator would also require a larger vessel.
3. Use two agitators in the existing reaction vessel to provide slightly better agitation.
4. Separate off a small section of the vessel which would incorporate a small agitator. Use this small section of the vessel to add the sulphuric acid to the slurry. Use a weir-type arrangement to overflow the mixed slurry (i.e. gypsum slurry) into the main reaction vessel and use the existing agitator to keep the solids in suspension.
5. Use a series of dip-tubes to add the sulphuric acid to the existing tank. Use 90° bends at the end of the tubes and extend the discharge points just under the agitator blade tips where the mixing intensity would be highest. The use of multiple acid discharge points within the reaction vessel has already been successful for ADM Southport.

Due to the time constraints of this research project, the options listed above were not investigated in detail and therefore allows the scope for further work in this area. Each of the possibilities should be researched in order to identify the modifications which would provide the greatest improvement to the sulphuric acid dispersion within the reaction vessel.

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Appendix A

Pannevis & Pressure Leaf Filters
Pannevis Filter

The pannevis filter consists of a slotted or perforated elastomer belt driven as a conveyor belt carrying a filter fabric belt. Both belts are supported by and pass across a support deck. A series of vacuum pans collect the filtrate. Slurry is fed at one end by an overflow weir and wash liquor is applied by weirs at a number of points as the belts travel along the deck. A schematic of a Pannevis filter is given in Figure A.1. The cake is discharged as the belt passes over the end pulley, where the filter medium belt is separated from the elastomeric drainage belt. From this point, each belt is returned to the feed point over a separate pulley. This procedure allows the filter medium belt to be washed thoroughly with sprays prior to rejoining the drainage belt. These filters have the advantages of the complete cake removal and the effective washing of the filter medium. The disadvantage is that at least half of the filter area is always idle on the return loop. Photographs of the pannevis filter in operation at ADM Ringaskiddy are shown in Figures A.2 and A.3. Figure A.2 illustrates a section of the filter just after one of the wash points. Figure A.3 illustrates the gypsum cake as it is about to separate from the filter belt and drop into a discharge chute.

Pressure Leaf Filter

The pressure leaf filter consists of flat filtering elements (leaves) supported in a pressure shell. A filter leaf consists of a heavy screen or grooved plate over which a filter medium of woven fabric or fine wire cloth is fitted. The leaves may be supported at the top, bottom, or centre and may discharge filtrate from any of these locations. The slurry enters in such a way as to minimize settling of the suspended solids. The shell is filled and filtration occurs on the leaf surfaces.
Appendix A

Photographs of the Pannevis Filter At ADM Ringaskiddy

Figure A.2: Pannevis Filter at ADM Ringaskiddy

Figure A.3: Pannevis Filter at ADM Ringaskiddy
Appendix B

Malvern Analysis, Histogram & Sieve Result Reports
Sample Details
Run Number: 2
Record Number: 11
Measured: 14 Apr 1997 14:21
Analysed: 14 Apr 1997 14:21
Result Source: Analysed

System Details
Beam Length: 2.40 mm
Sampler: MS1
Obscuration: 19.8 %

Result Statistics
Concentration = 0.0620 %Vol
Density = 1.000 g / cub. cm
Specific S.A. = 0.2828 sq. m / g

Size Low (um) | In % | Size High (um) | Under%  | Size Low (um) | In % | Size High (um) | Under%
---|---|---|---|---|---|---|---
0.05 | 0.00 | 0.06 | 0.00 | 6.63 | 1.44 | 7.72 | 6.25
0.06 | 0.00 | 0.07 | 0.00 | 7.72 | 1.74 | 9.00 | 7.98
0.07 | 0.00 | 0.08 | 0.00 | 9.00 | 2.04 | 10.48 | 10.02
0.08 | 0.00 | 0.09 | 0.00 | 10.48 | 2.35 | 12.21 | 12.37
0.09 | 0.00 | 0.11 | 0.00 | 12.21 | 2.71 | 14.22 | 15.08
0.11 | 0.00 | 0.13 | 0.00 | 14.22 | 3.14 | 16.57 | 18.22
0.13 | 0.00 | 0.15 | 0.00 | 16.57 | 3.70 | 19.31 | 21.92
0.15 | 0.00 | 0.17 | 0.00 | 19.31 | 4.40 | 22.49 | 26.32
0.17 | 0.00 | 0.20 | 0.00 | 22.49 | 5.26 | 26.20 | 31.58
0.20 | 0.00 | 0.23 | 0.00 | 26.20 | 6.23 | 30.53 | 37.82
0.23 | 0.00 | 0.27 | 0.00 | 30.53 | 7.24 | 35.66 | 45.06
0.27 | 0.00 | 0.31 | 0.00 | 35.66 | 8.16 | 41.43 | 53.22
0.31 | 0.00 | 0.36 | 0.00 | 41.43 | 8.90 | 48.27 | 62.12
0.36 | 0.00 | 0.42 | 0.00 | 48.27 | 9.46 | 56.23 | 71.58
0.42 | 0.00 | 0.49 | 0.00 | 56.23 | 8.72 | 65.51 | 80.30
0.49 | 0.00 | 0.58 | 0.00 | 65.51 | 7.29 | 76.32 | 87.59
0.58 | 0.00 | 0.67 | 0.00 | 76.32 | 5.50 | 88.91 | 93.09
0.67 | 0.03 | 0.78 | 0.03 | 88.91 | 3.71 | 103.58 | 96.79
0.78 | 0.04 | 0.91 | 0.07 | 103.58 | 2.18 | 120.67 | 98.98
0.91 | 0.05 | 1.06 | 0.13 | 120.67 | 1.02 | 140.98 | 100.00
1.06 | 0.07 | 1.24 | 0.20 | 140.98 | 0.00 | 163.77 | 100.00
1.24 | 0.09 | 1.44 | 0.28 | 163.77 | 0.00 | 190.80 | 100.00
1.44 | 0.11 | 1.68 | 0.39 | 190.80 | 0.00 | 222.28 | 100.00
1.68 | 0.13 | 1.95 | 0.52 | 222.28 | 0.00 | 258.95 | 100.00
1.95 | 0.16 | 2.28 | 0.68 | 258.95 | 0.00 | 301.68 | 100.00
2.28 | 0.21 | 2.65 | 0.89 | 301.68 | 0.00 | 351.46 | 100.00
2.65 | 0.27 | 3.09 | 1.16 | 351.46 | 0.00 | 409.45 | 100.00
3.09 | 0.37 | 3.60 | 1.53 | 409.45 | 0.00 | 477.01 | 100.00
3.60 | 0.51 | 4.19 | 2.04 | 477.01 | 0.00 | 555.71 | 100.00
4.19 | 0.59 | 4.88 | 2.73 | 555.71 | 0.00 | 647.41 | 100.00
4.88 | 0.91 | 5.69 | 3.64 | 647.41 | 0.00 | 754.23 | 100.00
5.69 | 1.16 | 6.63 | 4.80 | 754.23 | 0.00 | 878.67 | 100.00

Particle Diameter (um.)
Volume %

Result: Analysis Report
User Name: Catherine Shannon

Sample ID: TRIM TANK 14/4/97
Sample File: GYPSUM 2
Sample Path: C:\SIZERS\DATA\Sample Notes: PLANT SAMPLE

Result: Histogram Report

Sample Details
Run Number: 2
Record Number: 11
Measured: 14 Apr 1997 14:21
Analysed: 14 Apr 1997 14:21
Result Source: Analysed

Range Lens: 300RF mm
Beam Length: 2.40 mm
Presentation: 30HD
Analysis Model: Polydisperse
Modifications: None

System Details
Sampler: MS1
Obscuration: 19.8 %
Residual: 0.374 %

Result Statistics
Concentration = 0.0620 %Vol
Density = 1.000 g / cub. cm
Specific S.A. = 0.2828 sq. m / g
Uniformity = 5.588E-01

| Size (|Jm.) | Volume Over % | Size (|Jm.) | Volume Over % | Size (|Jm.) | Volume Over % |
|---|---|---|---|---|---|---|
| 0.055 | 0.06 | 0.635 | 100.00 | 0.700 | 99.99 |
| 0.061 | 0.06 | 0.722 | 99.97 |
| 0.067 | 0.06 | 0.851 | 99.95 |
| 0.074 | 0.06 | 0.938 | 99.92 |
| 0.082 | 0.06 | 1.03 | 99.88 |
| 0.090 | 0.06 | 1.14 | 99.84 |
| 0.099 | 0.06 | 1.26 | 99.79 |
| 0.109 | 0.06 | 1.39 | 99.74 |
| 0.121 | 0.06 | 1.53 | 99.67 |
| 0.133 | 0.06 | 1.69 | 99.60 |
| 0.147 | 0.06 | 1.86 | 99.52 |
| 0.162 | 0.06 | 2.05 | 99.43 |
| 0.178 | 0.06 | 2.26 | 99.32 |
| 0.196 | 0.06 | 2.49 | 99.20 |
| 0.217 | 0.06 | 2.75 | 98.94 |
| 0.239 | 0.06 | 3.03 | 98.78 |
| 0.263 | 0.06 | 3.34 | 98.66 |
| 0.290 | 0.06 | 3.69 | 98.39 |
| 0.320 | 0.06 | 4.07 | 98.06 |
| 0.353 | 0.06 | 4.48 | 97.68 |
| 0.389 | 0.06 | 4.94 | 97.26 |
| 0.429 | 0.06 | 5.45 | 96.64 |
| 0.473 | 0.06 | 6.01 | 95.97 |
| 0.522 | 0.06 | 6.63 | 95.20 |
| 0.576 | 0.06 | 7.31 | 94.31 |
| 0.635 | 0.06 | 8.06 | 93.30 |
| 0.700 | 0.06 | 8.89 | 92.17 |
| 0.772 | 0.06 | 9.80 | 90.91 |
| 0.851 | 0.06 | 10.81 | 89.54 |
| 0.938 | 0.06 | 11.91 | 88.03 |
| 1.03 | 0.06 | 13.14 | 86.36 |
| 1.14 | 0.06 | 14.49 | 84.57 |
| 1.26 | 0.06 | 15.97 | 82.58 |
| 1.39 | 0.06 | 17.62 | 80.37 |
| 1.53 | 0.06 | 19.42 | 77.92 |
| 1.69 | 0.06 | 21.42 | 75.17 |
| 1.86 | 0.06 | 23.62 | 72.09 |
| 2.05 | 0.06 | 26.04 | 68.64 |
| 2.26 | 0.06 | 28.72 | 64.79 |
| 2.49 | 0.06 | 31.66 | 60.53 |
| 2.75 | 0.06 | 34.92 | 55.86 |
| 3.03 | 0.06 | 38.50 | 50.80 |
| 3.34 | 0.06 | 42.45 | 45.41 |
| 3.69 | 0.06 | 46.81 | 39.72 |
| 4.07 | 0.06 | 51.62 | 33.72 |
| 4.48 | 0.06 | 56.92 | 27.68 |
| 4.94 | 0.06 | 62.76 | 22.02 |
| 5.45 | 0.06 | 69.21 | 16.89 |
| 6.01 | 0.06 | 76.32 | 12.41 |
| 6.63 | 0.06 | 84.15 | 8.69 |
| 7.31 | 0.06 | 92.79 | 5.71 |
| 8.06 | 0.06 | 102.3 | 3.44 |
| 8.89 | 0.06 | 112.8 | 1.84 |
| 9.80 | 0.06 | 124.4 | 0.71 |
| 10.81 | 0.06 | 137.2 | 0.04 |
| 11.91 | 0.06 | 151.3 | 0.00 |
| 13.14 | 0.06 | 166.8 | 0.00 |
| 14.49 | 0.06 | 183.9 | 0.00 |
| 15.97 | 0.06 | 202.8 | 0.00 |
| 17.62 | 0.06 | 223.6 | 0.00 |
| 19.42 | 0.06 | 246.6 | 0.00 |
| 21.42 | 0.06 | 271.9 | 0.00 |
| 23.62 | 0.06 | 299.8 | 0.00 |
| 26.04 | 0.06 | 330.6 | 0.00 |
| 28.72 | 0.06 | 364.6 | 0.00 |
| 31.66 | 0.06 | 402.0 | 0.00 |
| 34.92 | 0.06 | 443.3 | 0.00 |
| 38.50 | 0.06 | 488.8 | 0.00 |
| 42.45 | 0.06 | 539.0 | 0.00 |
| 46.81 | 0.06 | 594.3 | 0.00 |
| 51.62 | 0.06 | 655.4 | 0.00 |
| 56.92 | 0.06 | 722.7 | 0.00 |
| 62.76 | 0.06 | 796.9 | 0.00 |
| 69.21 | 0.06 | 878.7 | 0.00 |
| 76.32 | 0.06 | 951.8 | 0.00 |
| 84.15 | 0.06 | 1000.0 | 0.00 |

Particle Diameter (|Jm.)
System Details

Range Lens: 300RF mm  
Beam Length: 2.40 mm  
[Particle R.I. = (1.5295, 0.1000); Dispersant R.I. = 1.3300]

Sampler: MS1  
Dispersant R.I. = 1.3300

Obscuration: 19.8 %  
Residual: 0.374 %

Result Statistics

Distribution Type: Volume  
Concentration = 0.0620 %Vol

Mean Diameters:
D(v, 0.1) = 10.47 um  
D(v, 0.5) = 39.08 um  
D(v, 0.9) = 81.12 um  
Span = 1.808E+00

Specific S.A. = 0.2828 sq. m / g  
Uniformity = 5.688E-01

Mesh Aperture Volume No Volume Volume In% Below% In% Below%
10 2000 100.00 0.00 100.00
12 1700 100.00 0.00 100.00
14 1400 100.00 0.00 100.00
16 1180 100.00 0.00 100.00
18 1000 100.00 0.00 100.00
20 850 100.00 0.00 100.00
25 710 100.00 0.00 100.00
30 600 100.00 0.00 100.00
35 500 100.00 0.00 100.00
40 425 100.00 0.00 100.00
45 355 100.00 0.00 100.00
50 300 100.00 0.00 100.00
60 250 100.00 0.00 100.00

Volume %

0 10 20 30 40 50 60 70 80 90 100

0.01 0.1 1.0 10.0 100.0 1000.0

Particle Diameter (μm)
Appendix C

Malvern Reports to match Figures 4.6 & 4.7
Appendix C

MASTERSIZER

Result: Sieve BS 410:1986 Report

User Name: Catherine Shannon

Sample Details
Sample ID: CAKE #2 7/1/97
Sample File: GYPSPROJ
Sample Path: C:SIZERS\DATA\Sample Notes: PRIMARY STAGE FILTER OFF-LINE

Run Number: 1
Record Number: 45
Measured: 07 Jan 1997 10:51
Analysed: 07 Jan 1997 10:51
Result Source: Analysed

System Details
Range Lens: 300RF mm
Beam Length: 2.40 mm
Sampler: MS1

Presentation: 30HD

[Particle R.I. = (1.5295, 0.1000); Dispersant R.I. = 1.3300]

Analysis Model: Polydisperse
Modifications: None
Obscuration: 26.0 %
Residual: 0.388 %

Result Statistics
Distribution Type: Volume
Mean Diameters:
D [4, 3] = 34.43 \( \mu m \)

Concentration = 0.0672 %Vol
Density = 1.000 g / cub. cm
Specific S.A. = 0.3543 sq. m / g

D (v, 0.1) = 8.46 \( \mu m \)
D (v, 0.5) = 30.28 \( \mu m \)
D (v, 0.9) = 66.39 \( \mu m \)

Span = 1.913E+00
Uniformity = 5.967E-01

Mesh No | Aperture um | Volume In% | Volume Below%
--- | --- | --- | ---
10 | 2000 | 0.00 | 100.00
12 | 1700 | 0.00 | 100.00
14 | 1400 | 0.00 | 100.00
16 | 1180 | 0.00 | 100.00
18 | 1000 | 0.00 | 100.00
20 | 850 | 0.00 | 100.00
25 | 710 | 0.00 | 100.00
30 | 600 | 0.00 | 100.00
35 | 500 | 0.00 | 100.00
40 | 425 | 0.00 | 100.00
45 | 355 | 0.00 | 100.00
50 | 300 | 0.00 | 100.00
60 | 250 | 0.00 | 100.00

Mesh No | Aperture um | Volume In% | Volume Below%
--- | --- | --- | ---
60 | 250 | 0.00 | 100.00
70 | 212 | 0.00 | 100.00
80 | 180 | 0.00 | 100.00
100 | 150 | 0.00 | 100.00
120 | 125 | 0.56 | 99.44
140 | 106 | 1.77 | 97.67
170 | 90 | 3.82 | 93.85
200 | 75 | 5.83 | 88.02
230 | 63 | 7.76 | 80.26
270 | 53 | 8.63 | 71.63
325 | 45 | 9.52 | 62.11
400 | 38 | 100.00 | 100.00

Volume % vs Particle Diameter (\( \mu m \))
Result: Sieve BS 410:1986 Report

Sample Details
- Sample ID: TRIM 14/5/97
- Sample File: Gypsum 2
- Sample Path: C:SIZERS\DATA
- Sample Notes: SAMPLED ON PLANT.
- PH = 1.37
- Run Number: 3
- Recorded Number: 110
- Measured: 14 May 1997 15:44
- Analysed: 14 May 1997 15:44
- Result Source: Analyzed
- System Details
  - Range Lens: 300RF mm
  - Presentation: 30HD
  - Analysis Model: Polydisperse
  - Modifiers: None
  - Beam Length: 2.40 mm
  - [Particle R.I. = (1.5295, 0.1000), Dispersant R.I. = 1.3300]
  - Obscuration: 19.7 %
  - Residual: 0.807 %

Result Statistics
- Distribution Type: Volume
- Mean Diameters:
  - D [4, 3] = 59.59 um
- Concentration = 0.0868 %Vol
- Density = 1.000 g / cub. cm
- Specific S.A. = 0.2021 sq. m / g
- Span = 1.748E+00
- Uniformity = 5.301E-01

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Graphs and tables showing particle size distribution and volume percent.
Appendix D

Pump Calibration
# Pump Calibration Sheet I

**Pump Number**: 1  
**Pump Model Number**: 504 S  
**Liquid**: Calcium Citrate Slurry  
**Tube Bore Size**: 4.8 mm (Silicon)  
**Calibration Date**: 27th Feb. '97

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<th>Volume (mls)</th>
<th>Time (seconds)</th>
<th>Flowrate (ml/sec)</th>
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**Pump Calibration Sheet 2**

Pump Number: 2

Pump Model Number: 504 U

Liquid: Sulphuric Acid - 96% w/w

Tube Bore Size: 3.2 mm (Viton)

Calibration Date: 27th Feb. '97

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Appendix E

Overlay Malvern Plot
Appendix F

Pure Reactant Malvern Report

(2 peaks in distribution)
Result: Sieve BS 410:1986 Report

User Name: Catherine Shannon

Sample ID: RXN. 11/9/97
Sample File: GYPSUM 2
Sample Path: C:SIZERS\DATA\Sample Notes: 350g REACTANT FROM PLANT FILTER AND 12% W/W CITRIC. REACTED FOR ~ 28 HOURS. SOME REACTANT STILL EVIDENT IN MICROSCOPE ANALYSIS.

Sample Details

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Sample Details

User Name: Catherine Shannon

Sample ID: RXN. 11/9/97
Sample File: GYPSUM 2
Sample Path: C:SIZERS\DATA\Sample Notes: 350g REACTANT FROM PLANT FILTER AND 12% W/W CITRIC. REACTED FOR ~ 28 HOURS. SOME REACTANT STILL EVIDENT IN MICROSCOPE ANALYSIS.

Range Lens: 300RF mm
Beam Length: 2.40 mm
Particle R.I. = (1.5295, 0.1000)
Dispersant R.I. = 1.3300
Obscuration: 21.3%
Residual: 0.474%

Presentaton: 30HD
Analysis Model: Polydisperse
Modifications: None
Sampler: MS1

System Details

Distribution Type: Volume
Mean Diameters:
D(v, 0.1) = 9.19 um
D(v, 0.5) = 69.97 um
D(v, 0.9) = 141.21 um
D[4, 3] = 71.94 um
D[3, 2] = 12.23 um

Specific S.A. = 0.4905 sq. m / g
Uniformity = 6.015E-01

Result Statistics

Concentration = 0.0594 %Vol
Density = 1.000 g / cub. cm

Mesh Aperture Volume Below%

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Mesh Aperture Volume Below%

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Mesh Aperture Volume Below%

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Volume %

0.1 1.0 10.0 100.0 1000.0 10000.0

Particle Diameter (um)
Appendix G

Histogram Reports
Appendix G

Result: Histogram Report

User Name: Catherine Shannon

Sample ID: TRIM TANK 5/697
Sample File: GYPSUM 2
Sample Path: C:\SIZERS\DATA\Sample Notes: PLANT SAMPLE.

Range Lens: 300RF mm
Presentation: 30HD
Analysis Model: Polydisperse
Modifications: None

Beam Length: 2.40 mm
[Particle R.I. = (1.5295, 0.1000); Dispersant R.I. = 1.3300]
Sampler: MSI

Obscuration: 21.3 %
Residual: 0.441 %

Concentration = 0.0726 %Vol
Density = 1.000 g / cub. cm
Specific S.A. = 0.2643 sq. m / g
Span = 1.695E+00
Uniformity = 5.199E-01

Size (um) Volume Over %
0.055 100.00
0.061 100.00
0.067 100.00
0.074 100.00
0.082 100.00
0.090 100.00
0.099 100.00
0.109 100.00
0.121 100.00
0.133 100.00
0.147 100.00
0.162 100.00
0.178 100.00
0.196 100.00
0.217 100.00
0.239 100.00
0.263 100.00
0.290 100.00
0.320 100.00
0.353 100.00
0.389 100.00
0.429 100.00
0.473 100.00
0.522 100.00
0.576 100.00

Size (um) Volume Over %
7.31 95.07
8.06 94.20
8.09 93.24
8.90 92.00
9.01 91.00
11.91 89.82
13.14 88.46
14.49 86.97
15.87 85.30
17.62 83.41
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21.42 78.76
23.62 75.87
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92.79 20.00
102.3 16.00
112.8 12.00
124.4 8.00
137.2 4.00
151.3 0.00
166.8 0.00
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202.8 0.00
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539.0 0.00
594.3 0.00
655.4 0.00
722.7 0.00
796.9 0.00
878.7 0.00
### Result: Histogram Report

**Sample Details**
- **Sample D**: TRIM TANK 5/6/97
- **Sample File**: GYPSUM 2
- **Sample Path**: C:SIZERS\DATA1
- **Sample Notes**: PLANT SAMPLE FILTERED AND CAKE RETAINED.
  FILTRATE SPUN-DOWN AND LIQUID USED TO RE-SLURRY CAKE.
  FINE PARTICLES IN FILTRATE NOW ELIMINATED.

**System Details**
- **Range Lens**: 300RF mm
- **Presentation**: 3CHD
- **Analysis Model**: Polydisperse
- **Modifications**: None
- **Beam Length**: 2.40 mm
- **Sampler**: MS1
- **Dispersion**: (1.5295, 0.1000)
- **Dispersant R.I.:** 1.3300
- **Obscuration**: 28.0 %
- **Residual**: 0.389 %

**Result Statistics**
- **Distribution Type**: Volume
- **Mean Diameters**: D [4, 3] = 38.95 um
- **Concentration**: 0.0843 %
- **Density**: 1.000 g / cub cm
- **Span**: 1.848E+00
- **Specific S.A.:** 0.3103 sq. m / g
- **D (v, 0.1) =** 9.72 um
- **D (v, 0.5) =** 34.67 um
- **D (v, 0.9) =** 73.79 um
- **Span =** 5.748E-01

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<th>Size (um)</th>
<th>Volume Over %</th>
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**Chart:**
- **Particle Diameter (um):** 0.1 to 10.0
- **Volume %:** 0 to 100

**Measured:** 05 Jun 1997 14:46
**Analysed:** 05 Jun 1997 14:46
**Result Source:** Analysed

**User Name:** Catherine Shannon
**Security Level:** 1
Appendix H

Kenics Static Mixer
KENICS STATIC MIXER — STYLE KMR-PTFE
Appendix I

Lightnin’ A310 High Efficiency Impeller
A310 AXIAL FLOW IMPELLER
ONE PIECE HUB/BOLTED ON BLADES

NOTES:

1. WHEN ORDERING PARTS, SPECIFY DRAWING NUMBER, PART NAME, ITEM NUMBER, AND SERIAL NUMBER.

2. MINIMUM DIAMETER OPENING REQUIRED TO PASS DISASSEMBLED IMPELLER.